

THE GEOCHEMISTRY OF MANGANESE, IRON AND  
PHOSPHORUS IN AN ARCTIC LAKE

RECOMMENDED:

George W. Hipphut

U. Alen

Henry Joseph H. Sauer

F. Stuart Chapin, III

Robert J. Bandate

Chairman, Advisory Committee

John J. Laering

Head, Marine Science Program

U. Alen

Director, Division of Marine Sciences

APPROVED:

William S. Reelings

Vice Chancellor for Research and Advanced Study

7 October 83


Date

THE GEOCHEMISTRY OF MANGANESE, IRON AND  
PHOSPHORUS IN AN ARCTIC LAKE

A  
THESIS

Presented to the Faculty of the University of Alaska  
in Partial Fulfillment of the Requirements  
for the Degree of

DOCTOR OF PHILOSOPHY

 Science  
Library  
University of Alaska  
Fairbanks, Alaska 99701

By

JEFFREY CLAYTON CORNWELL, B.S.

Fairbanks, Alaska

December 1983

## ABSTRACT

Sediment redox processes were investigated in an oligotrophic, arctic lake containing metal oxide crusts in oxidizing surficial sediments (up to 22% Mn and 26% Fe). Toolik Lake, Alaska, a 12,000 year old kettle lake, has the lowest Pb-210 derived sedimentation rates reported for any lake ( $27 \text{ g m}^{-2} \text{ yr}^{-1}$ ).

Three independent methods for estimation of Mn, Fe and P retention within the lake (stream budgets, sediment traps and sediment burial rates) provide similar rates. Of the amounts entering the lake, 28% of P, 50% of Mn and 55% of Fe are retained. Common water column removal mechanisms for these elements and organic C are suggested by sediment trap data.

A steady state diagenetic model with terms for diffusion, reduction and oxidation shows that Mn and Fe crusts migrate within surficial sediments. Metal oxide burial rates are equivalent to oxide dissolution rates (reduction), rates of upward diffusion of soluble divalent metals and metal precipitation rates (oxidation). High inputs of labile Mn and Fe from streams, plus low sedimentation and organic matter oxidation rates are important for crust formation. Approximately 12% of Mn and 2% of acid reducible Fe retained by the lake since its formation exist as diagenetic oxides; the rest is buried within reducing sediment.

Sediment inorganic P migrates with Fe to form P enriched sediment zones with pore water  $\text{PO}_4$  concentrations beneath these zones regulated

by vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) formation. The migration of Mn and Fe within sediments results in the enrichment of Ba, Co, Ca, Ni, Ra-226 and carbonate in metal oxide enriched sediments. Barium is enriched in Mn crusts because of diagenetic migration.

## TABLE OF CONTENTS

	page
ABSTRACT .....	iii
TABLE OF CONTENTS .....	v
LIST OF FIGURES .....	viii
LIST OF TABLES .....	xii
ACKNOWLEDGEMENTS .....	xiv
CHAPTER 1. INTRODUCTION .....	1
<u>ARCTIC FRESHWATER CYCLING OF MN, FE AND P</u> ..	3
<u>SEDIMENT BIOGEOCHEMISTRY OF MN, FE AND P</u> ...	5
<u>STUDY AREA</u> .....	7
<u>TOOLIK LAKE: A UNIQUE GEOCHEMICAL ENVIRONMENT</u> .....	12
CHAPTER 2. STREAM AND WATER COLUMN STUDIES .....	15
<u>METHODS</u> .....	16
<u>WATER COLUMN CHEMISTRY</u> .....	20
<u>STREAM CHEMISTRY</u> .....	27
<u>PRECIPITATION CHEMISTRY</u> .....	35
<u>SEDIMENT TRAPS</u> .....	35
<u>STREAM AND LAKE BUDGETS</u> .....	39
<u>STREAM AND WATER COLUMN CONCLUSIONS</u> .....	47
CHAPTER 3. SOLID PHASE DISTRIBUTION OF MANGANESE, IRON AND PHOSPHORUS .....	48
<u>METHODS</u> .....	48
<u>RESULTS AND DISCUSSION</u> .....	50
Surficial Sediment .....	50
Vertical Distribution of Mn and Fe .....	57
Vertical Distribution of P .....	68

	page
<u>DEPOSITION VERSUS DIAGENESIS: CONTROL OF SOLID PHASE CHEMISTRY</u> .....	74
CHAPTER 4. LEAD-210 GEOCHRONOLOGY .....	76
<u>METHODS</u> .....	77
<u>CALCULATION OF SEDIMENTATION RATES</u> .....	79
<u>RESULTS</u> .....	83
<u>DISCUSSION</u> .....	89
<u>SUMMARY</u> .....	92
CHAPTER 5. CHEMICAL REACTION BETWEEN PORE FLUIDS AND LAKE SEDIMENT .....	93
<u>LIST OF TERMS USED IN CHAPTER 5</u> .....	93
<u>INTRODUCTION</u> .....	95
<u>METHODS</u> .....	98
<u>PORE WATER RESULTS</u> .....	101
<u>AUTHIGENIC MINERAL FORMATION</u> .....	108
Use of the Thermodynamic Approach:	
Applications and Limitations .....	108
Calculation of Ion Activity Products ....	109
Ion Activity Product Results .....	115
Authigenic Phases in Toolik Lake .....	117
Regulation of Pore Water Chemistry .....	121
Conclusions .....	122
<u>FORMATION OF METAL OXIDE CRUSTS:</u>	
<u>DIFFUSION/REACTION MODELLING</u> .....	123
Introduction to Diagenetic Models .....	123
Development of a Model .....	123
Manganese Diagenesis .....	128
Iron Diagenesis .....	136
<u>PHOSPHORUS DIAGENESIS</u> .....	142
<u>LIMITATIONS OF THE MODEL</u> .....	145
<u>METAL OXIDATION AND REDUCTION RATES:</u>	
<u>GEOCHEMICAL IMPLICATIONS</u> .....	146

	page
Manganese Reduction .....	146
Iron Reduction .....	153
Manganese Oxidation .....	153
Iron Oxidation .....	158
<u>CONTROL OF PORE WATER CHEMISTRY:</u>	
<u>CONCLUSIONS</u> .....	160
CHAPTER 6. TRACE ELEMENT DIAGENESIS AND DISTRIBUTION .....	162
<u>METHODS</u> .....	163
<u>RESULTS</u> .....	164
<u>DISCUSSION</u> .....	171
CHAPTER 7. MASS BALANCES AND CONCLUSIONS .....	177
<u>MANGANESE AND IRON GEOCHEMISTRY</u>	
<u>IN TOOLIK LAKE</u> .....	178
Manganese and Iron Budgets .....	178
Metal Oxide Rich Sediments: Putting	
Toolik Lake in Perspective .....	183
Metal Cycling and Organic Matter	
Oxidation .....	185
Evolution of Manganese and Iron Crusts ..	188
<u>THE TOOLIK LAKE PHOSPHORUS CYCLE</u> .....	191
<u>SUMMARY OF MAJOR FINDINGS</u> .....	193
<u>SUGGESTIONS FOR FUTURE RESEARCH</u> .....	195
REFERENCES .....	197
APPENDIX A. STREAM AND WATER COLUMN DATA .....	209
APPENDIX B. SOLID PHASE CHEMISTRY (1977-1979) .....	216
APPENDIX C. LEAD-210 DATA .....	220
APPENDIX D. PORE WATER CHEMISTRY AND ASSOCIATED SOLID	
PHASE DATA .....	224
APPENDIX E. TRACE ELEMENT DATA .....	231

# LIST OF FIGURES

	page
Figure 1-1. Toolik Lake watershed map with inset of Alaska.	8
Figure 1-2. Toolik Lake map showing depth contours and locations of water column and stream sampling sites.	10
Figure 2-1. 1980 water column TFe and DFe concentrations, contoured with lines of equal concentration ( $\mu\text{M}$ ).	22
Figure 2-2. 1980 water column DMn and PMn concentrations, contoured with lines of equal concentration ( $\mu\text{M}$ ).	23
Figure 2-3. Main inlet flow rates ( $\text{m}^3 \text{s}^{-1}$ ) for the 1978, 1980 and 1981 summer seasons.	29
Figure 2-4. Main inlet (IN1) and outlet (OUT) P concentrations. Solid lines are TDP and dashed lines are PP ( $\mu\text{M}$ ).	30
Figure 2-5. Main inlet (solid lines) and outlet (dashed lines) Fe concentrations ( $\mu\text{M}$ ).	32
Figure 2-6. Main inlet (solid lines) and outlet (dashed lines) Mn concentrations ( $\mu\text{M}$ ). Note the break in the DMn scale with maximum DMn of 4.48 $\mu\text{M}$ .	33
Figure 2-7. 1981 sediment trap P, Fe and Mn fluxes. Areal primary production estimates are from integration of C-14 uptake profiles. The daily sediment trap fluxes are the mean of two traps, with mean coefficients of variation less than 7.5%.	37
Figure 3-1. Map of Toolik Lake showing location of four cores (labelled with sampling depths). The other marked sites are surficial sediment locations.	51
Figure 3-2. Surficial chemistry showing: a. organic matter content as a function of water depth; b. total Mn content as a function of water depth; c. total P as a function of total Fe.	54



page

Figure 3-3.	Core T-18 chemistry. The core was collected in 1979 from 18 m depth in the lake's main basin. High concentrations of Mn and Fe take the form of crusts which cement sediment particles together.	58
Figure 3-4.	Core T-7 chemistry. The core was collected in 1978 from 7 m depth in the southeast side of the lake.	59
Figure 3-5.	Core T-5.5 chemistry. The core was collected in 1979 from 5.5 m depth near the lake's secondary inlet. The sediment surface was covered with an orange floc. Note the Mn scale change from the previous figures.	60
Figure 3-6.	Core T-4.5 chemistry. The core was collected in 1978 from the middle of the lake. <u>Nitella</u> covered the sediment surface.	61
Figure 3-7.	The redox parameter ( $pE + 3pH$ ) plotted as a function of depth for four cores. See text for an explanation of ( $pE + 3pH$ ).	67
Figure 4-1.	Sediment dilution by Mn and Fe oxides.	82
Figure 4-2.	Unsupported Pb-210 concentrations (normalized to Al concentration) plotted against cumulative Al. Four of the 12 cores are shown. The lines are linear regression best fits.	85
Figure 4-3.	Aluminum sedimentation rates in Toolik Lake, plotted with respect to overlying water depth. Error bars represent one SE. Cores from the west transect and east side of the lake are indicated.	86
Figure 4-4.	Radium-226 activity and Pb-210 data for the 18.0 m location. The peak in Ra-226 activity corresponds with high concentrations of sediment Mn and Fe in this core.	88
Figure 5-1.	Sediment reaction sequence for Toolik Lake profundal sediment. A series of sediment zones are indicated and potential reactions within each zone are presented.	97
Figure 5-2.	Pore water manganese data, 1980 transect. All concentrations in $\mu M$ .	102

	page
Figure 5-3. Pore water iron data, 1980 transect. All concentrations in uM.	103
Figure 5-4. Pore water phosphorus data, 1980 transect. All concentrations in uM.	104
Figure 5-5. Reddingite $pK_{sp}$ plotted against the ratio of $Fe^{2+}$ to $Mn^{2+}$ (Tessenow, 1974). The X's are pIAP values for the bottom 3 sections of all cores analyzed for interstitial water chemistry.	118
Figure 5-6. Solid phase P, Mn, Fe and carbonate plotted versus depth for the 18.0 m location.	119
Figure 5-7. Mn model parameters for T80-8.0 site.	129
Figure 5-8. Mn and Fe model output for the 18.0 m station.	137
Figure 5-9. Solid phase and interstitial P concentrations for two cores. The solid phase data have been normalized to the Al concentration.	143
Figure 5-10. First order dissolution of Mn. The log of the solid phase Mn concentration (from below the crusts and enriched zones) is plotted versus Pb-210 derived times, taking the Mn maximum as time zero.	148
Figure 5-11. The Mn dissolution K's are plotted versus the concentration of pore water Fe in each core. The Fe data was taken just below the region of Mn dissolution. The error bars show the maximum and minimum K's obtainable from adjacent points in Figure 5-10.	151
Figure 5-12. First order dissolution of Fe. The log of the solid phase Fe concentration (from below the crusts and enriched zones) is plotted versus Pb-210 derived times, taking the Fe maximum as time zero.	154
Figure 5-13. A plot of interstitial water data and model output for first order removal of Mn from solution. The best fit is for $K = 25 \text{ yr}^{-1}$ . See text for details.	156

	page
Figure 6-1. Major and trace metal data for core T80-18.0.	165
Figure 6-2. Major and trace element data for core T80-8.0.	166
Figure 6-3. Major and trace element data for core T79C-6.0.	167
Figure 6-4. Major and trace element data for core T80-5.5.	168
Figure 6-5. The range of concentration of major and minor metals in Toolik Lake cores, ferromanganese concretions from the Shebandowan Lakes (Sozanski and Cronan, 1979) and oxidate crusts from Lake Windermere (Gorham and Swaine, 1965).	169
Figure 6-6. Interstitial $Ba^{2+}$ and sediment Ba concentrations in cores from the 18.0 m location. The solid phase and pore water data are from different cores.	173
Figure 7-1. Manganese cycle for Toolik Lake.	179
Figure 7-2. Iron cycle for Toolik Lake.	180
Figure 7-3. Carbon cycle for Toolik Lake.	187
Figure 7-4. Dissolved $Mn^{2+}$ versus the concentration of solid phase Mn. These two parameters are significantly correlated ( $r=0.924$ , $p<0.01$ ).	190
Figure 7-5. Phosphorus cycle for Toolik Lake.	192

## LIST OF TABLES

	page
Table 2-1. Methods of stream and lake water analysis.	17
Table 2-2. Number of sampling dates per year.	19
Table 2-3. Toolik Lake water column chemistry.	21
Table 2-4. P, Mn and Fe concentrations (uM) in Toolik Lake and other arctic lakes.	24
Table 2-5. Toolik Lake stream chemistry.	28
Table 2-6. Precipitation chemistry.	36
Table 2-7. Watershed chemical export rates: high latitude environments.	40
Table 2-8. Toolik Lake stream budget.	42
Table 2-9. Atmospheric fluxes.	45
Table 2-10. 1981 sediment trap fluxes.	45
Table 3-1. Surficial sediment chemical maxima, minima and statistics.	52
Table 3-2. Molar ratios and correlation coefficients for total Fe:P, total Mn:P and total Fe:Mn in 4 cores and surficial sediments.	56
Table 3-3. Oxidative reactions for organic material of the Redfield composition (equations from Froelich <u>et al.</u> , 1979).	62
Table 4-1. Toolik Lake Pb-210 sedimentation.	80
Table 4-2. Sedimentation rates in North American lakes.	84
Table 5-1. Equilibrium constants at infinite dilution used in this study.	110
Table 5-2. Ion activity product data for core T80-18.0c.	114
Table 5-3. The pIAP values for the deepest sections of cores.	116
Table 5-4. Manganese reaction/diffusion model results.	131

	page
Table 5-5. Manganese fluxes in aquatic sediments.	134
Table 5-6. Iron reaction/diffusion model results.	138
Table 5-7. Iron fluxes in aquatic sediments.	139
Table 5-8. Reduction of manganese and iron; first order kinetic constants.	149
Table 7-1. Manganese and iron sedimentation; oxide crusts and permanent burial.	181

## ACKNOWLEDGEMENTS

A large number of individuals have been important to the design, field and laboratory work, and production of this dissertation. Dr. Robert Barsdate, my committee chairman, has guided this work since its inception, and taught me much about aquatic chemistry. The other members of my committee, Drs. Vera Alexander, Terry Chapin, George Kipphut and Joe Niebauer, have provided important feedback on the organization of this work, particularly its final stages. Dr. Sathy Naidu served on my committee prior to his sabbatical, and was always interested in my work and accessible to my questions. Dr. William Reeburgh gave me advice on pore water methods and encouragement at some of the more difficult times. Constant dialog on sediment geochemistry and Pb-210 geochronology with Dr. George Kipphut greatly improved the quality of this dissertation. Drs. Reeburgh, Burrell and Naidu generously allowed me access to equipment and instruments. Drs. Tom Blackburn and Bill Ahrnsbrak helped me to cultivate an interest in all things aquatic when I was an undergraduate.

A score of students and technicians associated with the project have aided in field and lab work. Steve Whalen collected many of the river samples and all of the sediment trap samples, and has provided data critical to this work. Dan McCorkle provided valuable field and lab assistance in the early stages of this work. There have been many other people that have shared good and bad times (from -40 to +20°C) through the years of field work: Tom Weingartner, Lew Molot, Keith

Muellor and many others.

Interaction with other students interested in geochemistry has made my graduate experience much more enjoyable and productive. Sound analytical advice from Sue Sugai has been essential to my work, as has her willingness to read the many drafts of this dissertation. Dave Glover analyzed samples for Ra-226 and Barry Spell did the Mo analyses. Malcom Robb provided important SEM and x-ray fluorescence data on sediment samples. The aquatic chemistry study group (Marc Alperin, Dave Glover, Sue Sugai, Sue Banahan, Dr. Richard Stolzberg and many others) helped to create an atmosphere conducive to geochemical research.

Excellent field support at Toolik Lake was provided by Dave Witt and other members of the Logistics Services staff. This research was funded from 1976 to 1978 by the Environmental Protection Agency (R804152-03) and from 1978 to 1980 by the National Science Foundation (DPP77-23475) as part of the Arctic Lake Process Study. State of Alaska fellowships provided key funding for this research (from 1980-1982), and I am grateful to the fellowship selection committee for their confidence in me. Logistic costs were borne by the NSF Arctic Lake Process Study and the Institute of Marine Science.

Finally, I would like to thank my parents for their understanding and encouragement despite long periods of separation and long distances between us. All stages of this dissertation and life in Alaska have benefitted from the encouragement and friendship of Sue Banahan.

## CHAPTER 1. INTRODUCTION

Iron and manganese, the two most abundant transition elements in the earth's crust, share an important property with the nutrient element phosphorus: the geochemical distribution of these elements in nature can be strongly influenced by environmental pE and pH. At high pE's, solid phase Mn(IV) and Fe(III) oxides are the thermodynamically stable forms of Mn and Fe, while at lower pE's they occur as reduced solution or solid phase Mn(II) and Fe(II). It is the greatly increased solubility of Mn and Fe under reducing conditions that makes these elements mobile in natural waters and allows their redistribution within a given sediment or water system. The adsorption of phosphate to Fe(III) oxides and hydroxides and the formation of Fe(II) and Mn(II) phosphate minerals exert significant control over the P concentrations in lake waters and sediments.

The purpose of this study is to describe and explain the distribution and transformations of Mn, Fe and P in Toolik Lake, an Alaskan arctic lake. Two general goals of this work are:

1. To broaden knowledge about the cycling of elements, particularly metals, in arctic freshwaters.
2. To increase understanding of the early stages of diagenesis (post depositional transformation) in aquatic sediments, particularly with respect to the cycle of Fe, Mn and P. It is hoped that this study will provide useful information for a more general understanding of sediment processes.



The choice of an arctic lake for the study of these processes may initially seem to pose excessive logistical problems that can limit one's ability to examine these processes. Such work in the arctic does, however, have some advantages. The late F. H. Rigler (1978a) best justified the extra effort and cost for the study of arctic lakes:

We are interested in arctic lakes first because they represent an extreme type, and study of the extremes often exposes or suggests general behavior patterns of our system that we would not discover by studying the more normal types. Second, we go to the Arctic, as we do to hot springs and salt lakes, in search of simplicity.

These two reasons apply very well to this study. For instance, the short thaw season and period of runoff to the lake enables comprehensive geochemical budgets to be calculated with less effort than would be necessary for lakes with longer flow seasons. During this study of sediment geochemistry, several advantages in the studying of diagenesis have been realized. Low organic productivity in both aquatic and terrestrial arctic environments results in oxic conditions in the lake water column and within the first few centimeters of lake sediment. The change from oxidizing to reducing sediments occurs as a continuum in this system, as it does in pelagic marine sediments (Froelich et al., 1979), and it is somewhat easier to recognize distinct sequences in early diagenetic processes. An absence of sulfate reduction occurs because of inadequate supplies of metabolizable

organic materials and the persistence of energetically more favorable electron acceptors during the oxidation of organic matter. This results in no significant removal of aqueous Fe(II) as inorganic sulfides. This provides an excellent opportunity for an examination of the importance of other inorganic ligands, such as phosphate and carbonate, in the regulation of Fe(II) concentrations in porewater.

The simplicity that Rigler cited can also reveal unrecognized complexity in some processes. The application of Pb-210 geochronologies to these sediments has resulted in a more complicated means of calculation of sedimentation rates; diagenetically formed oxides encrust and dilute surficial sediments. Post-depositional reactions redistribute trace metals in Toolik Lake sediments to a greater degree than is found in other environments.

#### ARCTIC FRESHWATER CYCLING OF P, MN AND FE

Of the three elements that comprise this study, only P has been studied extensively in arctic freshwaters, primarily because of its importance as a limiting nutrient. Detailed water column studies of nutrient elements have been undertaken in Barrow, Alaska ponds (Kalff, 1971; Prentki et al., 1980), Char and Meretta Lakes in the Canadian high arctic (Schindler et al., 1971a,b; de March, 1975;1978) and Oil Lake, Alaska (Miller et al., 1978; Barsdate, Cornwell and McCorkle, unpublished data), with less detailed studies and measurements made in arctic lakes and ponds by Kalff (1968), Kinney et al. (1972), Brunskill et al. (1973) and Mellor (1982). Subarctic lakes in Alaska

(Alexander and Barsdate, 1971; 1974; Barsdate and Alexander, 1971) and in Sweden (Personn et al., 1975) have also been studied. Of these studies, only the Char Lake data are relevant to deeper arctic lakes, since most of the other studies were not performed on arctic lakes, and they do not present detailed mass balance information necessary for the quantification of the P cycle. The Char Lake study showed low rates of P input from the watershed and from precipitation, and no discernable differences in P concentrations at different depths within the lake water.

Mass balances for Mn and Fe in arctic lakes had not been determined prior to this study. Iron was measured in Char Lake, but its cycle was not examined in detail. Measurements of Fe and Mn in other arctic lakes and ponds have been made, but not in the context of seasonal cycling or mass balances.

The cycles of these elements have been examined by measurement of the pool sizes and flux rates in streams, the water column, in sediment traps and via Pb-210 derived sediment accumulation rates. This study represents the first detailed work on Mn and Fe balances in an arctic lake, and one of the most complete metal balances for any lake. For P cycling, this work will parallel the Char Lake study, and provide the second mass balance in an arctic lake for this important nutrient element. Nutrient limitation by P is not examined in this study. The relative importance of N and P as limiting nutrients is not clear in this lake (S. Whalen, personal communication).

### SEDIMENT BIOGEOCHEMISTRY OF MN, FE AND P

The degradation of organic matter has a strong effect upon the chemical and microbial environments to which Mn, Fe and P are exposed upon burial in sediment. Organic matter oxidation proceeds via a series of coupled oxidation-reduction reactions in which electron acceptors (dissolved oxygen, nitrate, manganese(IV), iron(III) and sulfate) are successively reduced to produce the maximum free energy (Stumm and Morgan, 1981; Froelich et al., 1979; Reeburgh, 1983).

Major differences in the rate and quantitative importance of each of these coupled reactions are found in different sediments. For example, in the sediments of Griefensee (Emerson, 1976), the five reactions (all the way to sulfate reduction) occur in the top few centimeters of sediment. In pelagic marine sediments, dissolved oxygen can persist for tens of centimeters (Murray and Grundmanis, 1980), and the Mn reduction step in the organic matter oxidation scheme may commence at depths exceeding 40 cm (Froelich et al., 1979).

Most studies of lake sediment Mn, Fe and P cycling have been undertaken in reducing sediments where sulfate reduction and methanogenesis probably occur (Emerson, 1976; Emerson and Widmer, 1978; G.C. Holdren, 1977; Tessenow, 1974; and others). Toolik Lake has one of the most oxic sedimentary environments found in any lake, a result of low rates of sedimentation and low inputs of metabolizable organic matter. These sediments would be considered "post-oxic" in Berner's (1981) classification scheme because sulfate reduction is not attained. They are not as oxidizing as pelagic marine sediments, but

nevertheless represent an oxidized end member of lake sediments. In this lake, the dissolution of Mn(IV) and Fe(III) oxides under reducing conditions is followed by upward diffusion of aqueous Mn(II) and Fe(II), and in most cases, by accumulation of these reduced metals in oxidized zones at or below the sediment-water interface. The association of inorganic P with Fe(III) oxides (Williams et al., 1971) results in a redistribution of sediment P when Fe(III) is reduced (Carignan and Flett, 1981), and high concentrations of iron in interstitial solution result in the formation of reduced Fe(II) phosphates similar to those found in eutrophic lakes (Tessenow, 1974; Emerson and Widmer, 1978).

Toolik Lake has metal oxide crusts near the sediment-water interface and metal concentrations can exceed 20% Mn and 25% Fe; interstitial water Mn and Fe concentrations exceed 200  $\mu$ M. These crusts occur in accumulating sediments (as determined by Pb-210 dating), and appear to be caused by steady-state diagenesis. Numerical modelling of interstitial water chemical gradients, along with thermodynamic calculation of pore water solubility, will be used to examine the mechanisms of crust formation.

In the course of this study, data of many kinds were collected. All data collected in the course of this project are included in five appendices; the reader can have access to supporting data that researchers interested in data that has not been discussed in this dissertation (sediment N, major cations, Si, etc.) will have my data base to use as a starting point. Each appendix corresponds to the

data used in the five chapters in which new data are presented (Chapters 2 through 6).

### STUDY AREA

Toolik Lake ( $68^{\circ}38'N, 149^{\circ}38'W$ ) is located in arctic Alaska at an elevation of 720 m, in the northern foothills of the Brooks Range. The watershed includes glacial moraines and outwash left after the retreat of the Itkilik II glaciation, 12,000 to 14,000 yr ago (Hamilton and Porter, 1975; T.D. Hamilton, personal communication). The soils in the Toolik region are poorly drained with a peaty surface layer underlain by silt loams and silty-clay loams (Brown and Berg, 1980). Organic soils have low pH's (Brown and Berg, 1980; J. Cornwell, unpublished data), and the vegetation is mostly tussock tundra plants, with a high percentage of ground cover.

The Toolik watershed includes a series of small lakes, with Toolik Lake being the largest. Figure 1-1 shows the principle features of the watershed, which has an area of approximately  $65 \text{ km}^2$ , over forty times the area of Toolik Lake,  $1.5 \text{ km}^2$ . The main inlet stream drains 75% of the watershed, the second largest inlet 7% and a series of small streams on the lake's west side drain 18%. The Dalton Highway passes through the eastern side of the watershed, and a pipeline construction camp and a number of small gravel pads are found near the highway. Initial disturbance of the watershed by pipeline construction occurred in the late 1960's, although major construction activity started later.

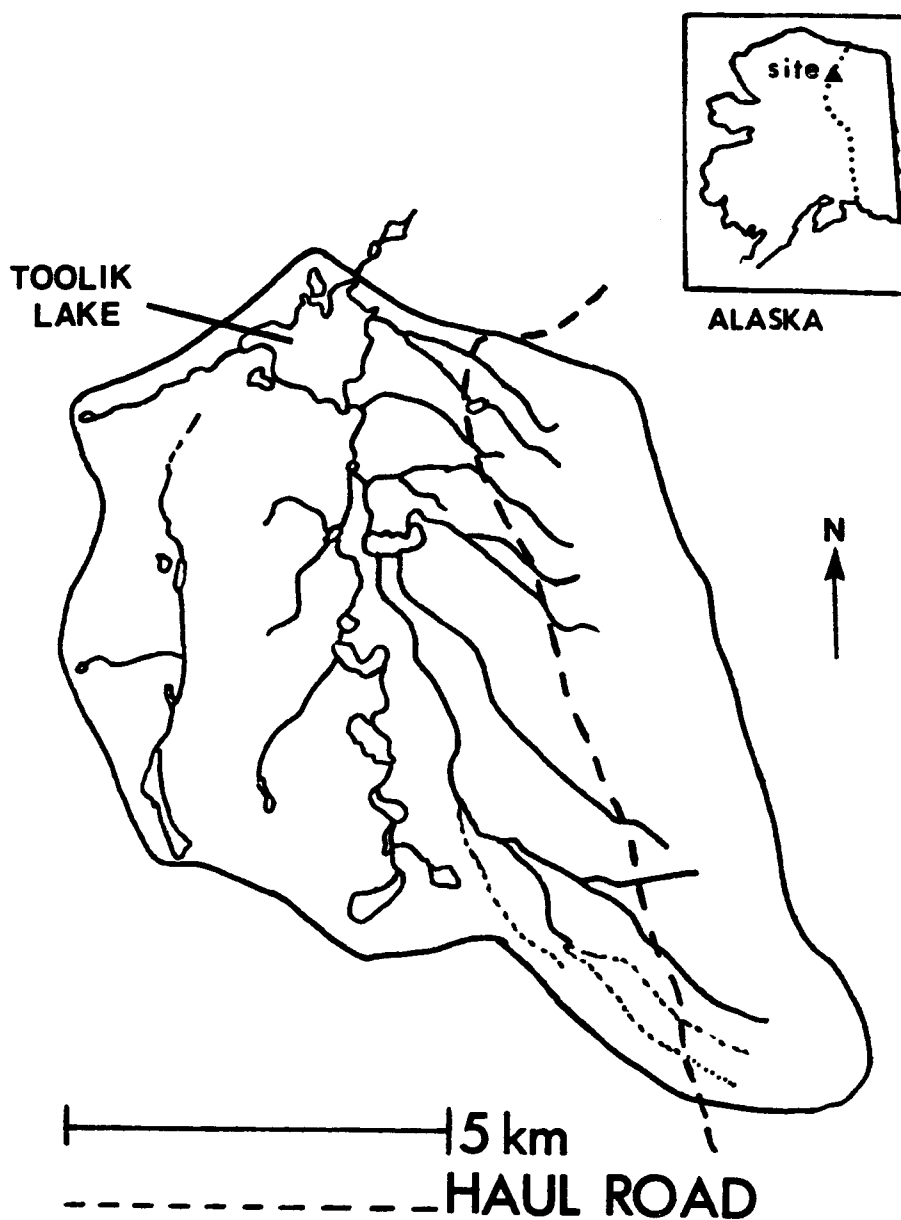


Figure 1-1. Toolik Lake watershed map with inset of Alaska.

The mean yearly temperature in the Toolik Lake region is  $-10^{\circ}\text{C}$ , with monthly temperatures less than  $-25^{\circ}\text{C}$  for the period December through March. Monthly average temperatures in July and August exceed  $10^{\circ}\text{C}$  (Brown and Berg, 1980). The mean yearly precipitation input is approximately  $20 \text{ cm yr}^{-1}$ , with equivalent amounts of frozen and unfrozen precipitation. Overall the climate is somewhat more continental than the arctic coastal plain, with a thaw season of 100 to 140 days (Brown and Berg, 1980).

Figure 1-2 shows a map of Toolik Lake. The complex lake morphometry results from the formation of distinct kettles by the retreat of glaciers and the melting of glacial ice. Five basins are separated by rocky shoals which come within 2.5 m of the lake surface. The lake margin consists of cobbles and boulders to depths of approximately 2.5 m, with fine grained sediments at greater depths. The mean depth of the lake is 7 m, with a maximum depth of 25 m. Nitella, mosses and epibenthic algae cover much of the sediment surface to depths of approximately 6 m.

Ice covers Toolik Lake from late September until late June, attaining a thickness of 100 to 140 cm. The lake is dimictic and mixes completely after ice-out and again in August and September. The summer thermocline occurs at depths of five to seven meters and water temperatures in the epilimnion reach  $16^{\circ}\text{C}$ .

Toolik Lake and other lakes, ponds, streams and rivers in the region have been the subject of multi-institutional studies since 1975. The Research on Arctic Tundra Environments (1975-1977) and the Arctic



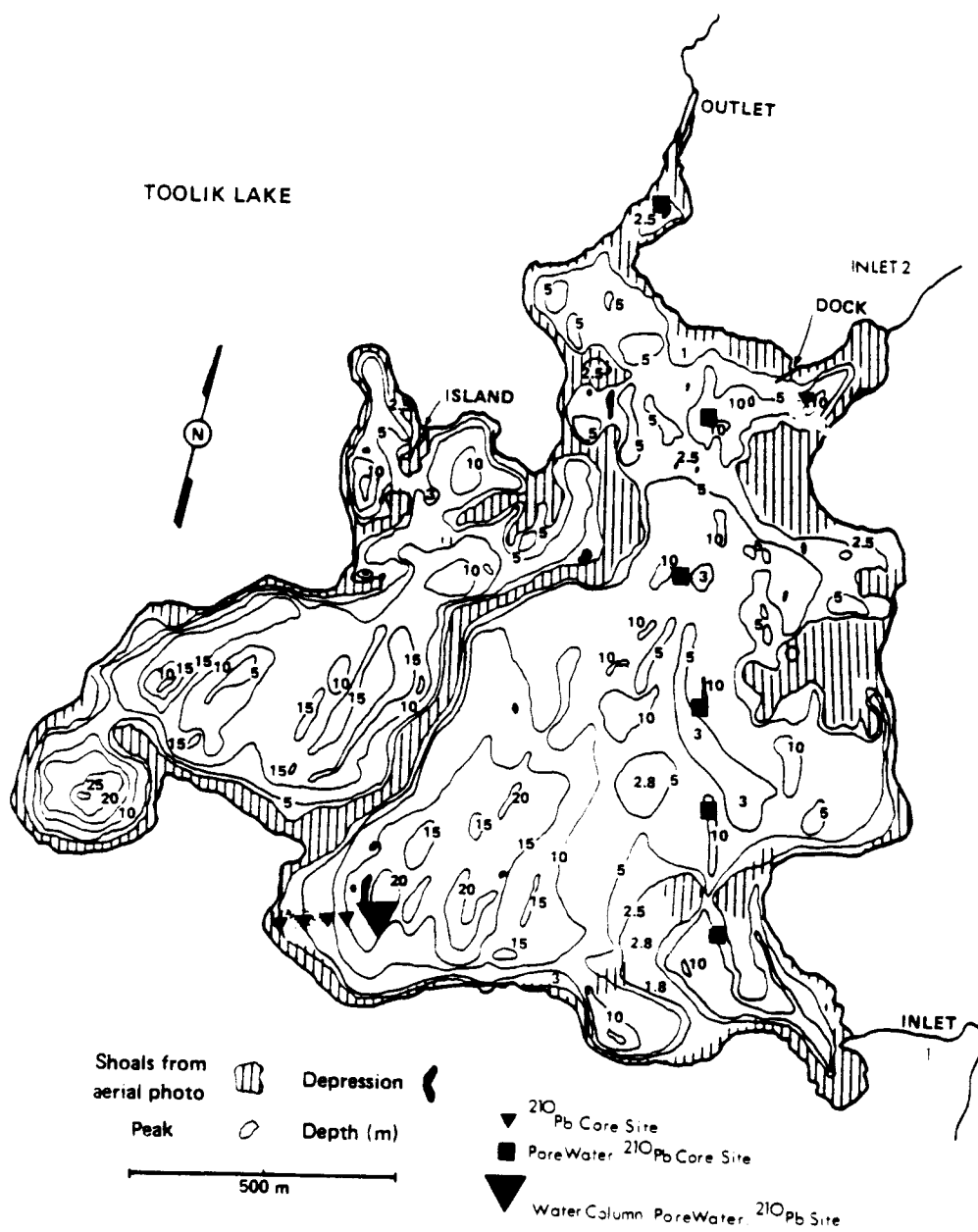


Figure 1-2. Toolik Lake map showing depth contours and locations of water column and stream sampling sites.

Lake Process Studies (1978-1980) programs have resulted in numerous theses and publications. A brief summary of some of the work will be presented.

Primary production in Toolik Lake was monitored for the period 1975 to 1981 by M.C. Miller and S. Whalen. High rates of primary production (up to  $270 \text{ mg C m}^{-3} \text{ d}^{-1}$ ) are found immediately under the ice during spring, with the highest areal rates (up to  $228 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) occurring in the first two weeks subsequent to ice-out (Miller et al., unpublished manuscript). Annual water column primary production averaged  $15 \text{ g C m}^{-2} \text{ yr}^{-1}$ . Bioassay work by Miller and Whalen (unpublished data) suggests that P is not the sole limiting nutrient in this lake, and that N limitation or combined N-P limitation may occur. Bacterial biomass in Toolik Lake is similar to that found in temperate lakes (Hobbie et al., 1983), and the highest bacterial numbers are thought to be a result of inputs from runoff water. Microbial degradation of plant litter in Toolik Lake proceeds at rates similar to that in other systems (Federle, 1981).

Klingensmith (1981) studied the N cycle in Toolik Lake sediments and found low levels (generally  $< 3.0 \text{ uM}$ ) of nitrate in sediment pore water. Concentrations of pore water ammonia reach  $50 \text{ uM}$  with exchangeable ammonia concentrations 5 to 20 times higher. Rates of nitrification and denitrification were estimated using tracer techniques. These experimental rates are in reasonable agreement with estimates determined via mass balances (Whalen and Cornwell, in prep.).

The zooplankton community in Toolik Lake has been studied by O'Brien et al. (1979) and Buchanan (1978) with regard to community structure and diel migration. Benthic studies by Mozley (unpublished) have shown that chironomids dominate the benthos in soft sediments, although total benthic population numbers are low, especially in profundal sediments. Cuker (1983) has examined the relationship between the production of benthic algae and snail grazing in the rocky littoral zone. Arctic grayling, lake trout, round whitefish, slimy sculpins and burbot comprise the fish community.

#### TOOLIK LAKE: A UNIQUE GEOCHEMICAL ENVIRONMENT

This study of Toolik Lake geochemistry covers a wide range of topics and because of the breadth of this dissertation, it may be hard to recognize what aspects of this study are unique. In this section, some of the important new findings are outlined and the chapters in which supporting data are found are referenced.

1. Terrestrial-aquatic interaction. This study of stream concentrations and watershed chemical export rates is the most detailed for any arctic watershed. The first comprehensive Mn and Fe stream data for high latitudes are included in this work. Watershed export rates are very low for all elements and the rates of cation export are the lowest on record, probably a result of low rates of chemical weathering. Large temporal variations in nutrient and metal concentrations were found. The relevant data are discussed in Chapter 2.
2. Lake retention of elements. Three independent methods for the

estimation of lake retention of Mn, Fe and P were used: stream budgets, sediment traps and sediment accumulation rates. For Mn and Fe, this represents the first comparison of these methods in any lake. The three methods agree very well for Mn and Fe, with moderate success for P. The data are discussed in Chapters 2 and 7.

3. Lead-210 sedimentation rates. The accumulation rate of sediment in Toolik Lake is lower than in any other lake study. A unique method of sedimentation rate calculation was made necessary by the dilution of sedimenting materials with Mn and Fe oxides of diagenetic origin. The data are discussed in Chapter 4.

4. Oxide crust formation. Toolik Lake has the highest concentrations of Mn and Fe found in any accumulating sediments. A simple reaction-diffusion model of Mn and Fe oxide crust formation works exceptionally well. The data are discussed in Chapter 5.

5. Authigenic vivianite formation. Vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) forms in the sediments of Toolik Lake despite low rates of P input and retention by the lake. Upward diffusion of phosphate with  $\text{Fe}^{2+}$  results in sediment horizons enriched in inorganic P which is adsorbed to Fe(III) oxyhydroxides. Below these solid phase enriched zones, pore water phosphate reaches concentrations many orders of magnitude higher than in the water column, and vivianite is precipitated. This is the first documented occurrence of authigenic vivianite in an extremely oligotrophic lake. The data are in Chapters 3 and 5.

6. Trace elements. The migration of Mn and Fe within sediments results in the enrichment of Ba, carbonate, Co, Mo and other trace

elements within more oxidizing sediment horizons. This is the clearest documentation of the enrichment of trace elements in lacustrine sediments because of association with metal oxides. The association of Ba with Mn (found in lacustrine ferromanganese concretions) results from diagenetic migration of Ba with Mn. The data are discussed in Chapter 6.

## CHAPTER 2. STREAM AND WATER COLUMN STUDIES

This examination of stream and water column Mn, Fe and P concentrations and fluxes has several goals:

1. To contribute to the general knowledge of concentrations of solutes in arctic freshwaters.
2. To examine the P cycle in Toolik Lake and to consider aspects of the P budget important to the regulation of primary production.
3. To use mass balance information for understanding processes such as watershed-stream interaction and water column removal of metals, which ultimately result in the formation of Mn and Fe enriched sediments.

In the context of the objectives of this study, the last goal is perhaps the most important. The other two reasons are of general interest to arctic limnology, and the data from Toolik Lake are among the most comprehensive found in the arctic literature. Although this dissertation is mostly restricted to the study of Mn, Fe and P, a complete set of analyses for dissolved and particulate organic C, water-color, suspended particulate weight and dissolved Na, K, Ca, Mg and Si were undertaken to better characterize lake chemistry. Alkalinity, pH, chlorophyll, organic and inorganic forms of N, water temperatures and light extinction have been measured by other investigators (Miller *et al.*, unpublished manuscript; S. Whalen, unpublished data).

Hobbie (1973) reviewed the early literature on the chemistry of arctic freshwaters. In the decade since then, only two major arctic

studies of chemical limnology have been undertaken, both under the auspices of the International Biological Program (IBP). The first study at Barrow, Alaska, dealt primarily with carbon and nutrient cycling in arctic coastal ponds (Hobbie 1980) and the second study involved two lakes in the Canadian high arctic, Char and Meretta lakes (Schindler et al., 1974a, 1974b; de March, 1975; Rigler, 1978a). Other data on arctic lake chemistry have consisted of measurements by Barsdate and Matson (1966), Kalff (1968), Kinney et al. (1972) and Brunskill et al. (1973).

Chemical measurements in this study were made in four general categories: the lake water column, inlet and outlet streams, precipitation and sediment traps. Stream flow measurements combined with chemical data provide the basis for mass balances.

#### METHODS

Water samples from Toolik Lake were obtained using messenger activated plastic sampling bottles. These were emptied into 4 L polyethylene bottles for transport to the laboratory. Care was taken to rinse these bottles with stream or lake water several times prior to sample storage.

At the laboratory, aliquots of these samples were measured out and filtered. Table 2-1 presents the abbreviation used for each analysis, as well as the filters, mode of preservation and analytical methods used for water and particulate analysis throughout this study. Filtrates were stored in weak acid (HCl) cleaned polyethylene bottles

Table 2-1. Methods of stream and lake water analysis.

Analysis	Name	Filter	Preservation	Preparation	Final Analysis	References
total dissolved P	TDP	Gelman A/E	freeze	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + heat	colorimetry	A,B
particulate P	PP	Gelman A/E	freeze	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + heat	colorimetry	A,B
total Fe	TFe	none	HCl	NH <sub>2</sub> OH HCl	colorimetry	C,D
dissolved Fe	DFe	Nuclepore 0.4 u	HNO <sub>3</sub>	NH <sub>2</sub> OH HCl	colorimetry	D
dissolved Mn	DMn	Nuclepore 0.4 u	HNO <sub>3</sub>	none	graphite tube AAS	
particulate Mn	PMn	Nuclepore 0.4 u	dry	NH <sub>2</sub> OH HCl	flame AAS	
silicic acid	Si	Gelman A/E	freeze	none	AutoAnalyzer	E
particulate organic C	POC	ashed Gelman A/E	freeze	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + heat	IR analyzer	F
dissolved organic C	DOC	ashed Gelman A/E	freeze	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + heat	GC	F,G
Ca, Mg		Gelman A/E	HNO <sub>3</sub>	lanthanum	AAS	H
Na, K		Gelman A/E	HNO <sub>3</sub>	none	AAS	H
watercolor (350 nm)		Gelman A/E	freeze	none	colorimetry	
suspended sediment	WT	Nuclepore 0.4 u	freeze	dry @ 65°C	electrobalance	
stream flow					Gurley meter	I
dissolved oxygen		none			titration	J
total alkalinity		none			titration	J

A. Strickland and Parsons (1968)

F. Loder (1971)

B. Menzel and Corwin (1965)

G. Stainton (1973)

C. Murray et al. (1978)

H. U.S. EPA (1974)

D. Gibb (1979)

I. Hobbie et al. (1983)

E. Armstrong et al. (1967)

J. American Public Health Association (1974)



after two rinses with filtrate.

The coefficients of variation of the Mn and P measurements are all less than 15% for samples with low concentrations ( $<0.1 \mu\text{M}$ ), with substantially better coefficients of variation at higher concentrations. The mean coefficient of variation for the Fe analyses is less than 3% for DFe, with slightly higher coefficients of variation for TFe. Stream flow estimates made with a transect of Gurley meter flow measurements across streams average 87% of those using dye dilution techniques (Hobbie *et al.*, 1983).

An overview of major lake and stream sampling during the course of this project is presented in Table 2-2. The water column data for 1976 and 1977 were collected during all seasons, with water column data for subsequent years restricted to the summer months. The 1976 and 1977 data were collected as part of a separate research project not directly associated with this thesis, but the data are presented in Appendix A to provide background information on Toolik Lake chemistry. Stream flow data for 1978 were provided by J. Hobbie and co-workers, and stream sample collection in 1980 and 1981 was a joint effort with S. Whalen. All sediment trap samples were provided by S. Whalen, who used two 16.2 cm diameter traps following the handling procedures of Kirchner (1975).

The only exceptions to the information provided in Table 2-1 occurred in 1978. The PP and particulate iron (PFe) analyses employed perchloric acid for digestion of glass fiber filters, and TFe is the sum of DFe and PFe.

Table 2-2. Number of sampling dates per year.

Analysis	1976	1977		1978		1980		1981
	Lake	Lake	Stream	Lake	Stream	Lake	Stream	Stream
TDP	5	11	11	9	17	6	19	14
PP	5	10	11	9	17	6	19	14
TFe	-	-	-	-	16	7	19	14
DFe	-	-	-	-	-	6	19	14
DMn	-	-	-	-	-	6	19	14
PMn	-	-	-	-	-	6	19	14
Si	-	-	-	-	-	6	19	-
DOC	-	-	-	-	-	6	19	14
POC	-	-	-	-	-	6	19	-
Na,K,Ca,Mg	-	-	-	6	23	6	19	-
Water Color	-	-	-	-	23	6	19	-
WT	-	-	-	-	-	6	19	-
Dissolved O <sub>2</sub>	2	8	-	6	-	-	-	-
Stream flow	-	-	-	-	25	-	19	14

The acid-reductant method used for TFe and PMn analysis was performed using lake sediments to determine whether or not this technique yielded results comparable to harsher ( $\text{LiBO}_2$ ) digestions. The recovery of Fe via the water column technique was approximately 50% of total sediment Fe, indicating that the water column technique may not detect up to half of the Fe entering the lake. Sediment manganese recovery via the acid reducible technique was 100%. From these results, it appears that the Fe budget should be considered the budget for acid reducible Fe.

#### WATER COLUMN CHEMISTRY

A summary of concentrations of major elements in Toolik Lake is presented in Table 2-3. Calcium is the dominant cation, comprising 75% of the positive charge, and bicarbonate is the major anion, comprising 66% of the negative charge. Sulfate and chloride were not determined in this study, but the difference between cations and bicarbonate is approximately 210  $\mu\text{M}$  of negative charge. Dissolved organic carbon concentrations and water color are quite high in this lake and some of the missing negative charge may be provided by organic anions. The water column remains oxic throughout the year, although one smaller basin has significant dissolved oxygen consumption during the winter (M. C. Miller *et al.*, unpublished manuscript).

Water column concentrations of P are low year round, with 1980 mean water column concentrations ranging from 0.06  $\mu\text{M}$  to 0.12  $\mu\text{M}$  for PP, and from 0.11 to 0.25  $\mu\text{M}$  for TDP. As in the Char Lake study

Table 2-3. Toolik Lake water column Chemistry. All concentration are  $\mu\text{M}$  (except pH).

Element	Low Value <sup>a</sup>	High Value <sup>a</sup>	"Typical Value" <sup>b</sup>
Ca	210	280	230
Mg	55	70	60
Na	17	25	22
K	5	10	8
Si	24	38	29
$\text{HCO}_3^-$	320	500	400
POC	9	57	25
DOC	530	780	630
Dissolved $\text{O}_2$	150	330	280
pH	6.5	7.2	6.8

<sup>a</sup> the low and high values are those encountered for individual samples excluding samples immediately under the ice which are higher or lower than the median water column concentrations depending upon the season.

<sup>b</sup> the typical value presented here is for the period of time immediately after ice-out. These values are the volume weighted mean values for the lake.

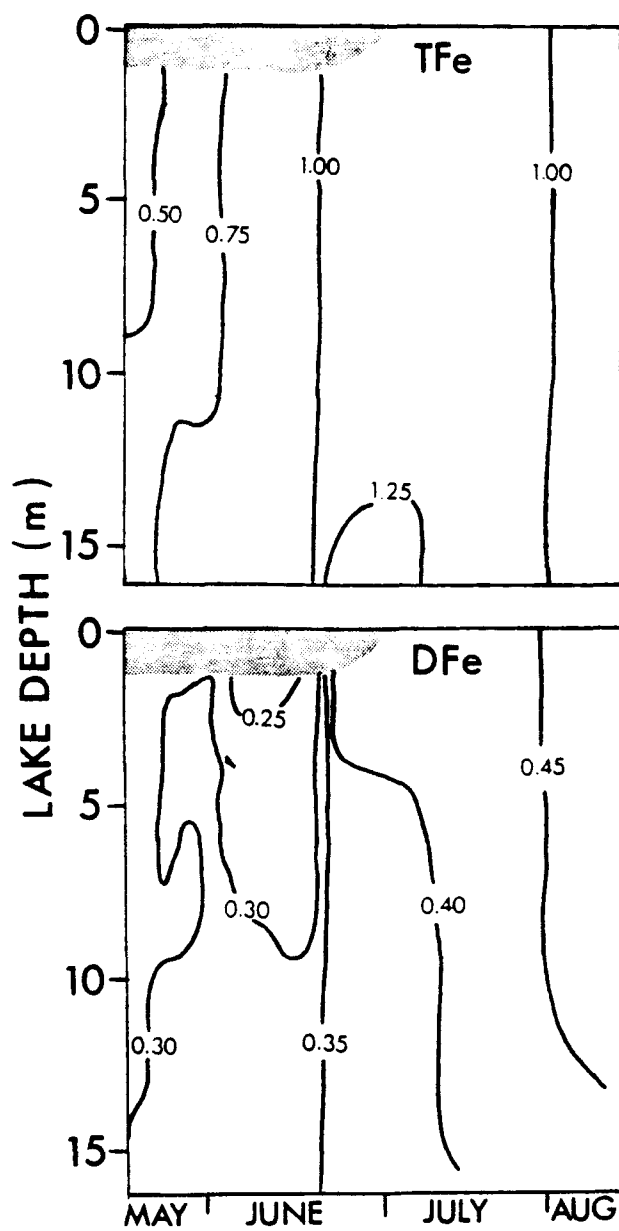


Figure 2-1. 1980 water column TFe and DFe concentrations, contoured with lines of equal concentration ( $\mu\text{M}$ ).

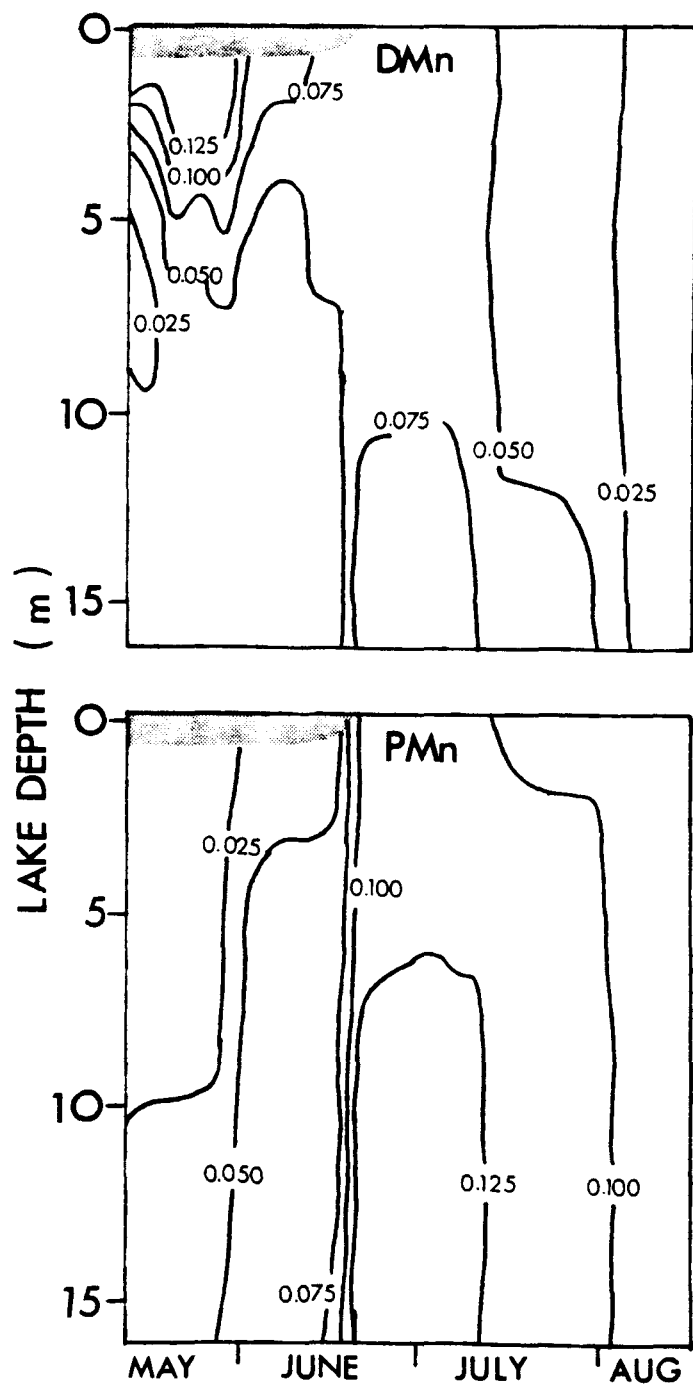


Figure 2-2. 1980 water column PMn and DMn concentrations, contoured with lines of equal concentration ( $\mu\text{M}$ ).

Table 2-4. P, Mn and Fe concentrations (uM) in Toolik Lake and other arctic lakes.

Site	Phase	P			Fe			Mn			Ref.
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Toolik Lake	dissolved	0.09	0.59	0.11	0.07	0.52	0.40	0.015	0.286	0.027	this work
	particulate	0.03	0.18	0.12	0.14	1.07	0.79	0.004	0.146	0.012	
Char Lake	dissolved	-	-	0.06	-	-	0.02	-	-	-	A
	particulate	0.03	0.16	0.06	-	-	-	-	-	-	
Arctic Coast	dissolved	-	-	-	-	-	2.47	0.035	0.060	-	B
	particulate	-	-	-	-	-	1.54	0.084	0.546	-	
Arctic	dissolved	-	-	-	-	-	0.27	0.015	0.027	-	B
	particulate	-	-	-	-	-	0.87	0.015	0.027	-	
Brooks Range	dissolved	-	-	-	-	-	0.43	-	-	0.018	B
	particulate	-	-	-	-	-	5.21	-	-	0.120	
MacKenzie Delta	dissolved	0.13	12.	-	0.17	29.	-	0.0	18.	-	C
	particulate	0.19	33.	-	-	-	-	-	-	-	
Barrow Ponds	dissolved	-	-	0.45	3.9	13.7	-	-	-	-	D
	particulate	-	-	0.33	-	-	-	-	-	-	

- References:
- A. de March, 1975; Schindler et al., 1974
  - B. Barsdate and Matson, 1966; Hobbie, 1973
  - C. Brunskill et al., 1973
  - D. Prentki et al., 1980

(Schindler et al., 1974a), no distinct seasonal trends for PP and TDP were found. In 1980, the average water column TFe concentration increased from 0.43 uM on May 13 to 1.19 uM on 1 July, decreasing to 0.53 uM on 28 October. Dissolved Fe ranged from 31 to 56% of total Fe during the summer months. Most of the change in TFe throughout the summer be accounted for by changes in the PFe concentration (Figure 2-1). Figure 2-2 shows the concentrations of DMn and PMn in 1980. High concentrations of DMn in the water immediately beneath spring ice show that streams and direct runoff are important sources of Mn for Toolik lake. The highest concentrations of DMn are found in May, with concentrations decreasing throughout the season. Particulate Mn has its maximum in early July.

As in lakes from other regions of the world, arctic lakes show large variations in the concentrations of dissolved and particulate Mn, Fe and P (Table 2-4). The mean concentrations of TDP and PP in Toolik Lake are somewhat higher than in Char Lake, but generally lower than found in the MacKenzie Delta lakes (Brunskill et al., 1973) and Barrow Ponds (Prentki et al., 1980). An absence of vertical structure in P concentrations is found in Toolik Lake and in other arctic lakes (Schindler et al., 1974a; R.J. Barsdate, unpublished data). The importance of P in limiting primary production in high latitude lakes has been demonstrated by increased production associated with P additions (Schindler et al., 1974b; Personn et al., 1975) and in significant P-chlorophyll correlations for many lakes (Personn et al., 1975; Nicholls and Dillon, 1978; and others). Low levels of TDP are



consistent with the low productivity found in Toolik Lake (Miller et al., unpublished manuscript), although similarly low levels of inorganic N may actually lead to nitrogen limitation (S. Whalen, personal communication). The biological availability of TDP for lake biota was not characterized in this study because measurement of dissolved "reactive" P is difficult at low levels. The analytical method may overestimate the concentration of the "available" species by the hydrolysis of some organic P compounds (Stainton, 1980). Attempts to analyze reactive P on frozen samples gave extremely variable results, with most concentrations less than 0.06  $\mu\text{M}$ . Analysis of fresh samples at Toolik Lake in 1979 indicated that no analytically detectable reactive P existed within the lake during summer, even when low level techniques were applied (Strickland and Parsons, 1968).

The largest increases in DMn and DFe concentrations in lakes occur as a result of decreasing pE, and most studies of these metals have been in lakes in which elevated concentrations of Mn and Fe are found in anoxic hypolimnia (Verdouw and Dekkers, 1980; Davison, 1982; Kelley et al., 1982). Differences between the concentrations of DMn and DFe at mid-depths and those in bottom water are quite low, suggesting that sediments are not a large source of Toolik Lake water column Mn and Fe.

## STREAM CHEMISTRY

This discussion of stream input-output processes will be based upon 1980 as a model year because only in 1980 was the first week of flow sampled. This first week can have an overwhelming impact on the budget of some elements.

Table 2-5 presents a summary of the concentrations in the main inlet in 1980. With the exception of TDP, TFe, DFe, PMn and DMn, the stream concentrations are similar to those in the water column. These forms of P, Fe and Mn are all found in higher concentrations in the main inlet than within the lake (using a flow corrected mean stream concentration).

The flow of water into the lake from the main inlet (Figure 2-3) has large variations within a given year and between different years. Large fluxes of water into the lake are found during spring runoff, and large inputs are also found throughout the summer season after precipitation. Observations from pipeline workers in 1978 indicated that an early melt occurred in late April of that year, suggesting that the total amount of water input into the lake was higher than the amount measured. Logistic problems in 1981 resulted in no samples being collected during the first 10 days of spring runoff, providing a low estimate of water and elemental inputs.

High PP and TDP concentrations were found during the beginning of spring flow (Figure 2-4), both in the main inlet and in the outlet. The absence of early season data accounts for the lower concentrations in

Table 2-5. Toolik Lake stream chemistry. The data are for the main inlet in 1980, with all concentrations in  $\mu\text{M}$  except WT which is in  $\text{mg L}^{-1}$  and  $\text{H}_2\text{O}$  which is  $\text{m}^3 \text{s}^{-1}$ . %Early is the percentage of total yearly input of each element which enters the lake in the first 10% of the summer flow season. The time correlation is significant at 99% confidence: a positive correlation means that concentrations increase significantly throughout the summer. The relative to the water column category is a comparison of the weighted mean for stream concentrations with the typical concentrations encountered in the water column. Weighted mean stream concentrations are calculated by dividing the total yearly input of the element ( $\mu\text{mol}$ ) by the total yearly input of water ( $\text{L}$ ).

Analysis	Low	High	Mean	S.D.	%COV	Weighted Mean	%Early	Time Correlation	Relative to Lake Water Column
PP	0.02	0.50	0.12	0.14	117	0.08	43	negative	=
TDP	0.06	1.08	0.31	0.26	84	0.24	26	negative	greater
TFe	1.58	4.23	2.29	0.64	28	2.32	16	none	much greater
DFe	0.73	2.20	1.38	0.36	26	1.34	14	none	much greater
PMn	0.014	0.166	0.054	0.038	70	0.045	24	negative	greater
DMn	0.047	4.478	0.485	1.031	213	0.388	72	none	much greater
POC	7.	108.	38.	28.	74	29.	25	negative	=
DOC	533.	1167.	674.	178.	26	625.	13	negative	=
Si	11.4	41.3	24.4	7.7	32	26.2	11	none	=
Na	13.	24.	19.	3.	16	19.	9	none	less than
K	3.	54.	11.	12.	109	7.	33.	none	=
Ca	105.	292.	199.	54.	27	200.	8	positive	less than
Mg	25.	67.	49.	11.	22	50.	9	positive	less than
WT	0.13	6.23	1.36	1.57	115	0.91	34	none	=
$\text{H}_2\text{O}$	0.31	4.47	1.44	1.08	75	1.47	10	none	

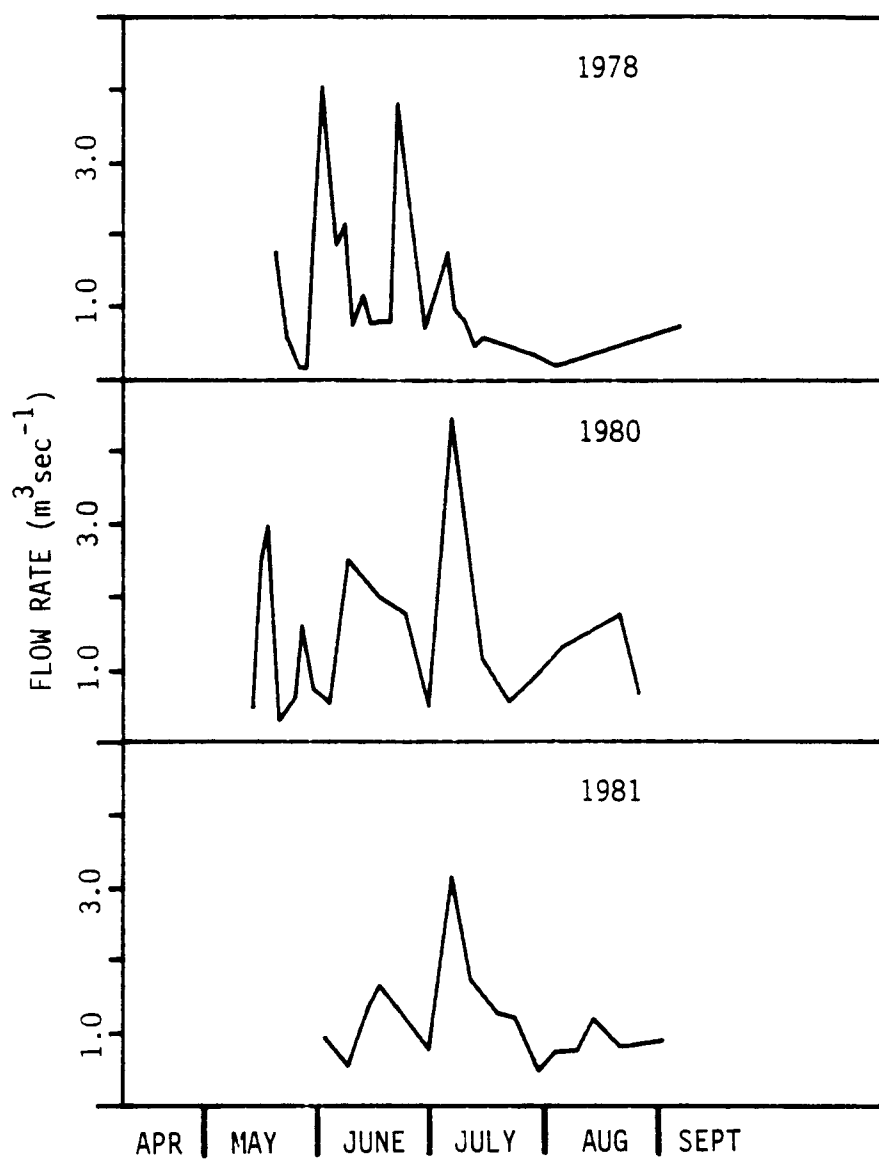


Figure 2-3. Main inlet flow rates ( $\text{m}^3 \text{s}^{-1}$ ) for the 1978, 1980 and 1981 summer seasons.

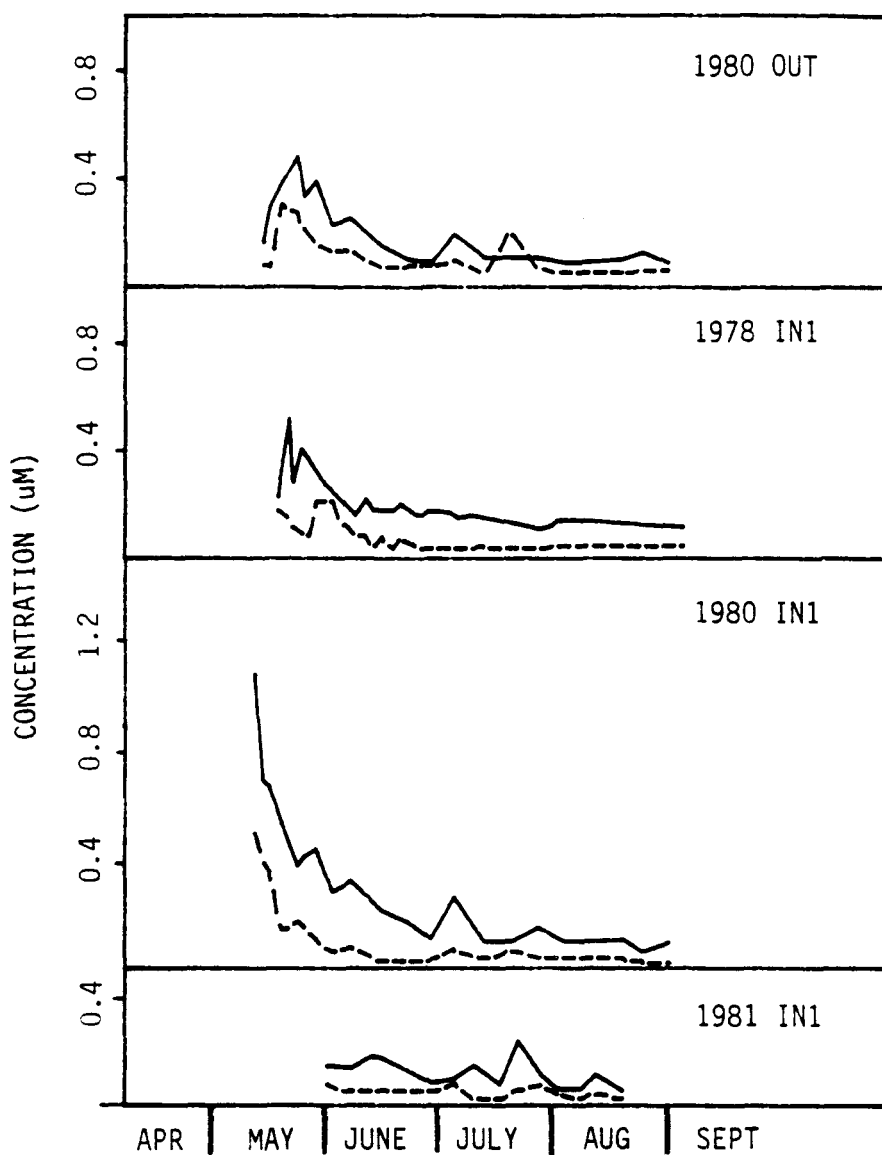


Figure 2-4. Main inlet (IN1) and outlet (OUT) P concentrations. Solid lines are TDP and dashed lines are PP (uM).

1978 and 1981. Limited sampling in 1977 shows high PP and TDP concentrations during early May. High spring inputs of P were absent in Char Lake (Schindler et al., 1974a) and P concentrations were somewhat lower than that at Toolik, especially for TDP.

The concentrations of TFe and DFe are usually lower in the lake water and outlet than in the inlet (Figure 2-5), suggesting retention of Fe by the lake. The highest concentrations of TFe and DFe in both inlet and outlet streams are found during spring runoff. Dissolved Fe comprised 58 and 61% of TFe in the main inlet and 55 and 47% of TFe in the outlet, for 1980 and 1981 respectively.

The most striking feature of Mn input is the high concentration of DMn during the first week of flow (Figure 2-6). A smaller peak in DMn concentration occurs in the lake outlet several days later. After the first 10 days of spring runoff, PMn concentrations in the outlet exceed that of the inlet. High DMn concentrations were found at the same time in the secondary inlet, although DMn concentrations only reached 1.11 uM.

Higher concentrations of Mn, Fe and P are found in the outlet during the first two weeks of spring flow. Elevated concentrations of Mn, Fe and P under the lake ice show that inflowing melt water does not mix completely with the lake, but is remaining somewhat undispersed under the ice. Dye flow studies (Hobbie et al., 1983) have shown that water generally flows along the eastern side of the lake. Dye appeared in the outlet within five days after its addition to the inlet. Schindler et al. (1974a) found a similar early season flow

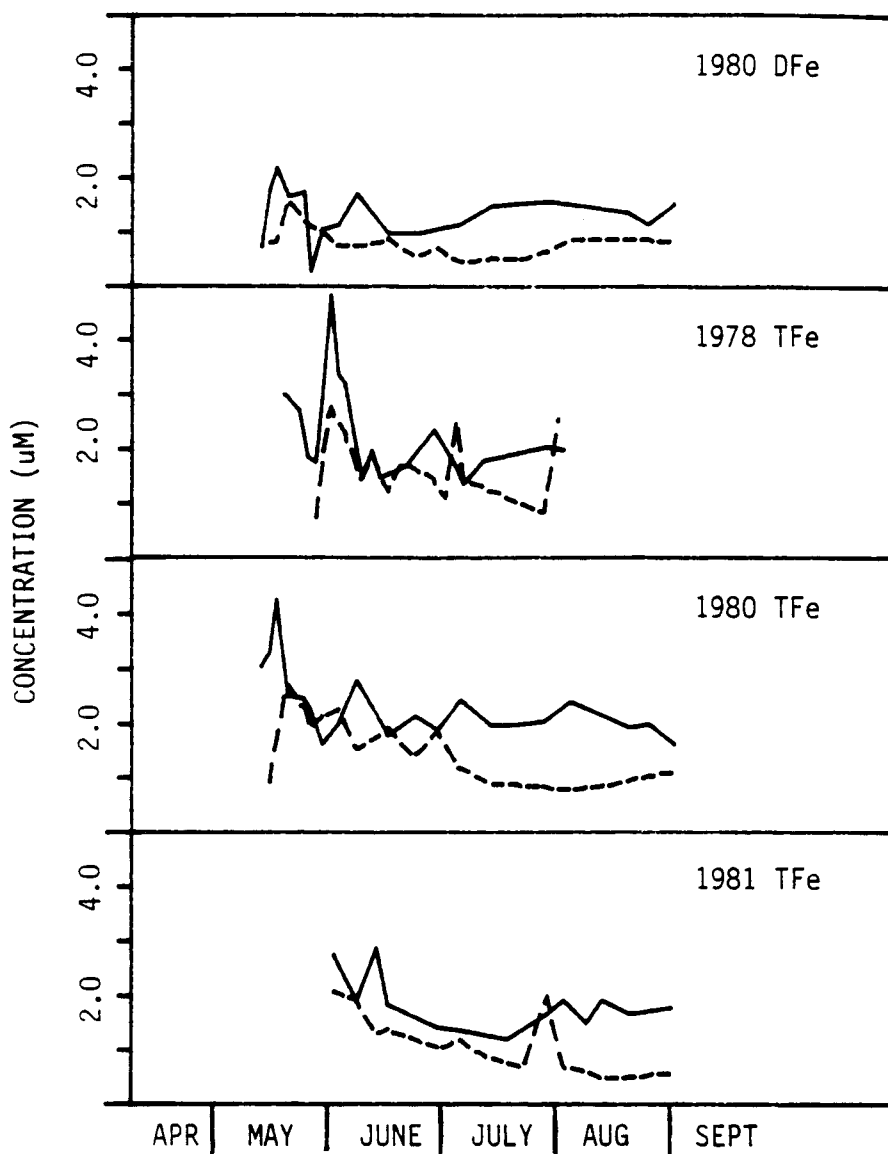


Figure 2-5. Main inlet (solid lines) and outlet (dashed lines) Fe concentrations (uM).

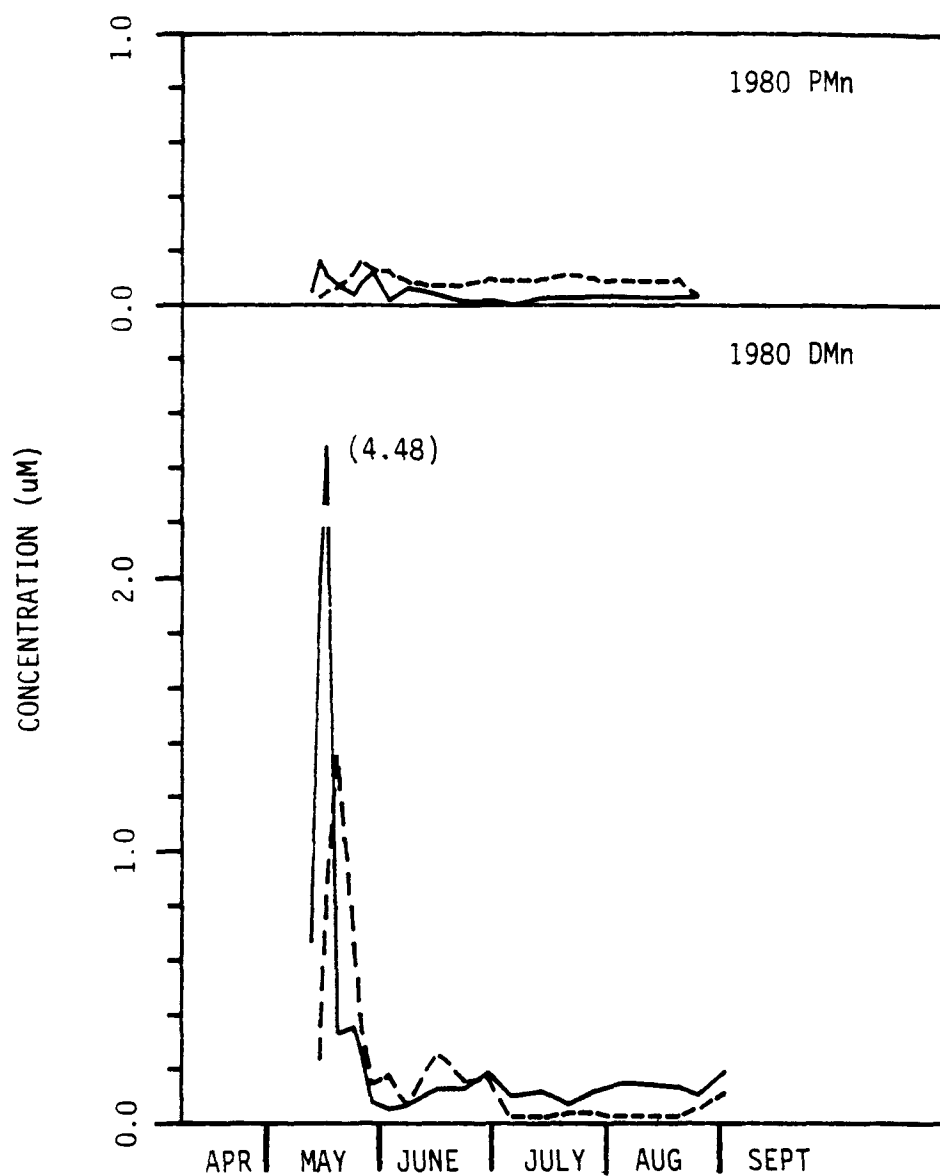


Figure 2-6. Main inlet (solid lines) and outlet (dashed lines) Mn concentrations (uM). Note the break in the DMn scale with maximum DMn of 4.48 uM.



pattern for Char Lake. Several small streams enter Toolik Lake during summer, and on 6 July 1980 most chemical parameters were measured on four of these streams. Small streams generally have lower TDP, DFe and DMn concentrations than the main inlet, and higher particulate concentrations.

Correlation matrices were computed for each set of inflow or outflow data to examine the relationship between the different parameters. The 1980 main inlet data set will be used as an example of this kind of analysis. Of the 21 variables examined (including the N data of S. Whalen), 78 significant ( $p < 0.01$ ) correlations were found. Two important findings of this correlation analysis are:

1. Stream flow rates have little influence on the concentrations of elements. Many solute and particulate concentrations are high during spring flow, but concentrations do not change greatly later in the season, even when water flow rates exceed those of spring flow.
2. A large number of stream parameters decrease during the course of the season, including PP, TDP, PMn, POC, DOC, K,  $\text{NO}_3^-$  and both particulate and dissolved organic N. Only Ca and Mg increase during the summer season. Table 2-5 indicates significant correlations ( $p < 0.01$ ) between concentration and the number of days after spring flow commenced.

The large variation in flow has an impact on the daily mass transport rates of solutes and particulates, but concentrations seem relatively unaffected. One of the major findings of this study is that a large fraction of the annual budget of Mn, P and several other

elements enter Toolik Lake during the first 10 days of the flow season (Table 2-5).

#### PRECIPITATION CHEMISTRY

Precipitation was collected a number of times during the course of this study (Table 2-6). In 1977 and 1978, the concentration of P was determined on snow samples from within the Toolik watershed. Snow samples from 1980 and 1981 were taken from on top of the lake ice at the onset of spring melt. These samples were quite wet at the time of collection, and some direct runoff of water from the tundra may have occurred. Precipitation samples from 1981 were supplied by S. Whalen. The P concentrations (Table 2-6) are similar to those at Barrow, Alaska (Prentki et al., 1980) and at Char Lake (Schindler et al., 1974a; de March, 1975).

Complete chemical analyses were performed on five snow samples from 1980. Relative to the water column, DMn and all particulate parameters are enriched, and remaining solutes are low. High PFe, PP and PMn concentrations are associated with high concentrations of particulate material in snow. Total particulates in snow increased in the vicinity of tundra which had been blown clear of snow, indicating the importance of local terrestrial sources of particulates.

#### SEDIMENT TRAPS

Sediment trap data are useful for looking at both the character and quantity of material which is being sedimented out of the euphotic zone. Figure 2-7 shows the 1981 sediment trap data plotted on a

Table 2-6. Precipitation chemistry. All concentrations are  $\mu\text{M}$ .

Location		N	PP	TDP	Na	K	Ref.
Toolik	snow 1977	6	$0.39 \pm 0.12$	$0.26 \pm 0.11$	-	-	
Lake	snow 1978	5	-	$0.22 \pm 0.15$	$12 \pm 2$	$2 \pm 1$	
	snow 1980	5	$0.50 \pm 0.32$	$0.14 \pm 0.06$	$9 \pm 5$	$1.5 \pm 0.5$	
	snow 1981	3	$0.27 \pm 0.09$	$0.06 \pm 0.05$	-	-	
	rain 1981*	8	$0.33 \pm 0.27$		-	-	
Char	snow		-	0.19	35	5	A
Lake	rain		-	0.32	35	5	
Barrow	winter		0.05	0.08	-	-	B
	summer		-	0.25	-	-	
Char	snow		0.35	0.31	-	-	C
	rain		0.43	0.52	-	-	

Location		N	PFe	DFe	PMn	DMn
Toolik	snow 1980	5	$5.0 \pm 2.8$	0.05	$0.11 \pm 0.13$	$0.27 \pm 0.11$

\* No filtration was performed. Concentration is total P.

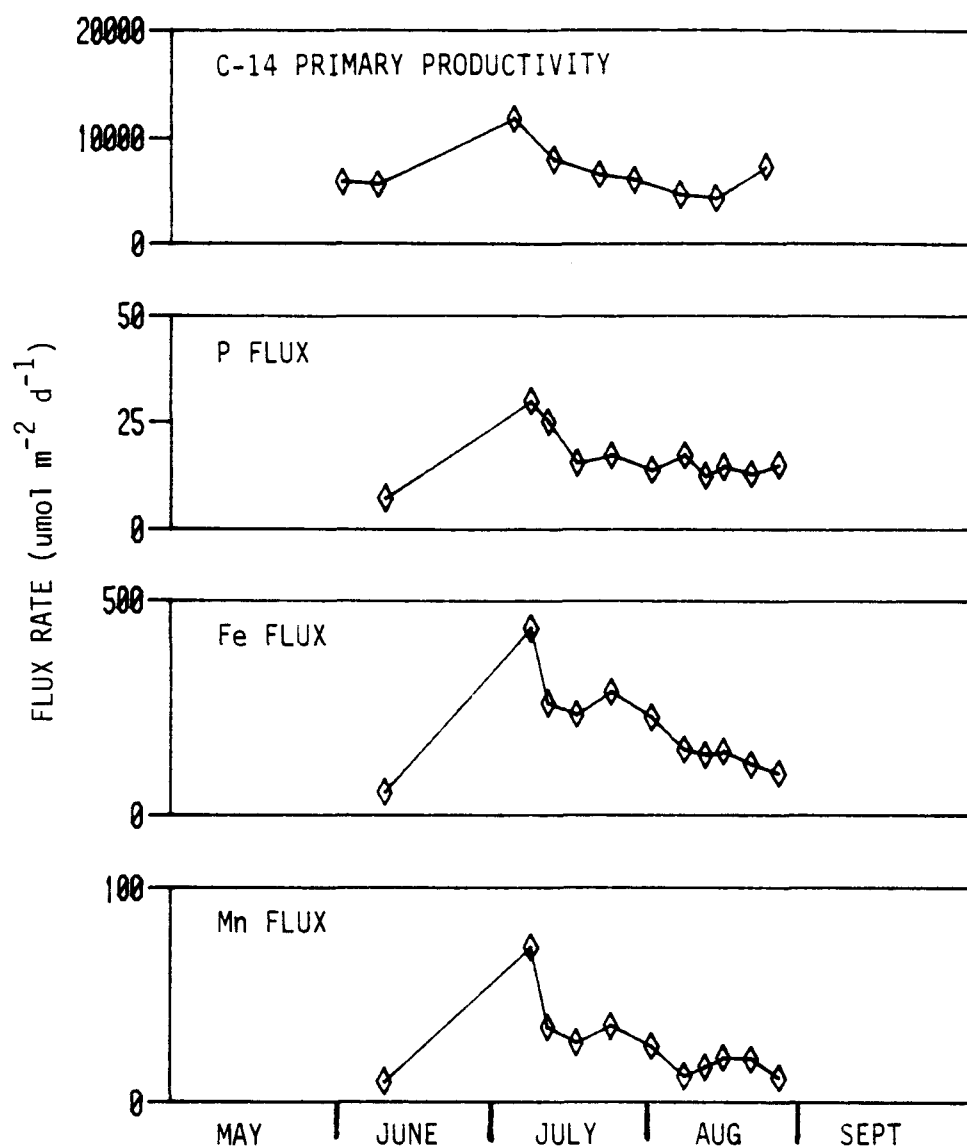


Figure 2-7. 1981 sediment trap P, Fe and Mn fluxes. Areal primary production estimates are from integration of C-14 uptake profiles. The daily sediment trap fluxes are the mean of two traps, with mean coefficients of variation less than 7.5%.

seasonal basis. The productivity data was supplied by S. Whalen. The similarity of all four plots is quite apparent. On the basis of these data, it would appear that Mn, Fe and P deposition rates are controlled by similar mechanisms. Nitrogen follows a similar seasonal trend (S. Whalen, unpublished data).

Dean and Greeson (1979) hypothesized that phytoplankton concentrate dissolved Mn and Fe into the particulate phase in Oneida Lake, leading to water column removal of these elements. Barsdate and Matson (1966) demonstrated that dissolved Mn uptake by arctic lake particulates was higher in natural samples than in killed controls, again suggesting a biological mechanism for metal removal. Chapnick et al. (1982) have implicated Mn oxidizing bacteria in the removal of dissolved Mn from the Oneida Lake water column. The correspondence of the highest rates of water column removal of metals with peak rates of primary production and nutrient element sedimentation suggests that biological processes may influence the removal of metals from the water column.

### STREAM AND LAKE BUDGETS

Budgets for nutrients and other elements in terrestrial and aquatic ecosystems can be of great value in understanding biogeochemical processes (Likens et al., 1977; Rigler, 1978b; Vollenweider, 1976). Budgets may be used to estimate and compare loss rates of P, Mn, Fe and other elements from the watershed, and to investigate lake retention of these elements. Vollenweider (1976) has emphasized the utility of mass balances for the understanding of lake ecosystem functioning.

The terrestrial export data presented in Table 2-7 are for the main inlet watershed only. Approximately 80% of the stream input to Toolik Lake enters via this inlet. The effect of several smaller lakes upstream from Toolik Lake on the character of main inlet water has not been determined, but they may lower concentrations of suspended particulates in the water which flows into Toolik Lake. The rates of loss of P from the terrestrial ecosystem are similar for both Toolik and Char Lakes. Plant cover in the Char Lake watershed is only 5 to 7% (Schindler et al., 1974a), as compared to almost complete coverage in the Toolik Lake watershed (Brown and Berg, 1980). Particulate P makes up a higher fraction of TP in the Char Lake streams, perhaps because of poorer stabilization of soils. These TP export rates are not much lower than that found for forest watersheds of the Canadian Shield (Dillon and Kirchner, 1975), but are much lower than in most other watersheds.

High amounts of DOC enter Toolik Lake via streams. The watershed

Table 2-7. Watershed chemical export rates: high latitude environments. All rates are  $\text{mmol m}^{-2} \text{yr}^{-1}$  except for the water flux, which is  $\text{cm yr}^{-1}$ .

Location	TP	PP	TDP	TFe	PFe	DFe	TMn	PMn	DMn
Toolik 1978	0.032	0.010	0.022	0.43	-	-	-	-	-
1980	0.091	0.022	0.069	0.66	0.28	0.38	0.122	0.014	0.109
1981	0.032	0.010	0.022	0.34	0.13	0.21	0.027	0.013	0.014
Char 1971	0.045	0.030	0.015	0.02	-	-	-	-	-
1972	0.098	0.059	0.039	-	-	-	-	-	-
1973	0.072	0.035	0.035	-	-	-	-	-	-
MacKenzie -lo		0.030	0.050						
Delta -hi		3.7	0.66	-	-	-	-	-	-
Blossom R.	-	-	0.20*	7.5	-	-	0.35	-	-
Wilson R.	-	-	0.18*	6.1	-	-	0.21	-	-

Location	Na	K	Ca	Mg	Si	water
Toolik 1978	3.5	1.4	28	6.9	-	18
1980	5.4	1.9	56	14.1	7.4	30
1981	4.8	0.7	35	8.2	-	18
Char 1971	42.	11.7	97	32.	1.2	-
1972	-	-	-	-	-	-
1973	-	-	-	-	-	-
MacKenzie -lo	16.	2.1	42	24.	1.1	-
Delta -hi	55.	9.2	309	156.	19.2	-
Blossom R.	-	-	250	-	62.	-
Wilson R.	-	-	120	-	22.	-

Location	TC	POC	DOC	References
Toolik 1978	-	-	-	
1980	184.	8.2	176	this study
1981	-	-	-	
Char 1971	-	-	4.3	Schindler <i>et al.</i> , 1974
1972	30.7	1.6	29.	de March, 1975
1973	11.1	1.1	10.	de March, 1975
MacKenzie -lo	-	325.	-	
-hi	-	3.6	-	Brunskill <i>et al.</i> , 1973
Blossom R.	-	-	700.	
Wilson R.	-	-	1100.	Sugai and Burrell, 1983

\* reactive P

DOC export rate is higher than for Char Lake. The Toolik Lake total organic C export value is virtually identical ( $176 \text{ mmol m}^{-2} \text{ yr}^{-1}$  versus  $187 \pm 81 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) to the mean value given by Mulholland and Watts (1982) for seven large Alaskan watersheds, most of which were subarctic.

Comparison of the metal export rates from the Toolik Lake watershed is made difficult by the paucity of data from other ecosystems. The Fe export rate is approximately 20 times higher than that of Char Lake, but 10 times less than that found in southeast Alaska rivers (Sugai and Burrell, 1983). The 1980 Mn export rate at Toolik Lake is 30 to 50% of that found in southeast Alaska rivers. The major cation export rates are among the lowest found in any ecosystem, and are lower than the rates presented by Likens et al. (1977) for a large number of ecosystems.

Low rates of physical and chemical weathering in this watershed are responsible for low export rates. Precipitation is low, there are only about 100 to 140 days of thawing conditions each year and the permafrost thaws down to only 0.5 m (Brown and Berg, 1981). Physical disintegration of rock and subsequent transport of this material by streams occurs very slowly, as evidenced by the low suspended solids content of the streams. Much of the suspended material (up to 70%) is organic matter. The low rates of solute export indicate that chemical weathering is slow.

The export of Fe from the watershed is enhanced by the presence of dissolved humic substances, which maintain Fe in solution in



Table 2-8. Toolik Lake stream budget. The units for water input are  $\text{m}^3 \text{yr}^{-1}$  (multiply the values shown by  $10^6$ ) in place of kmol, and  $\text{m} \text{yr}^{-1}$  instead of  $\text{mmol m}^{-2} \text{yr}^{-1}$ . TOT/LA and NET/LA are the loading and retention rates per unit lake area. %RETAINED is the % of total stream input retained by the lake and XTRA is a synthetic input for water not accounted for by the two major inlets.

Year	ID	$\text{kmol yr}^{-1}$					$\text{mmol m}^{-2} \text{yr}^{-1}$			%RETAINED
		IN1	IN2	XTRA	OUT	INTOT	NET	TOT/LA	NET/LA	
1978	PP	0.82	-	0.07	1.01	0.89	-0.12	0.60	-0.081	-
	TDP	1.68	-	0.14	1.69	1.82	0.13	1.22	0.089	-
	TP	2.50	-	0.21	2.70	2.71	0.01	1.82	0.008	-
1980	PP	1.08	0.19	0.39	1.82	1.66	-0.16	1.12	-0.11	-
	TDP	3.34	0.48	1.07	3.01	4.89	1.88	3.28	1.26	-
	TP	4.42	0.67	1.46	4.83	6.55	1.72	4.40	1.15	26
1978	TFe	20.9	-	1.8	17.6	22.7	5.1	14.2	3.5	22
1980	PFe	13.4	1.0	3.1	10.9	17.5	6.6	11.8	4.5	-
	DFe	18.4	1.9	5.0	13.3	25.3	12.0	17.0	8.1	-
	TFe	31.8	2.9	8.1	24.2	42.8	18.6	28.8	12.6	44
1981	TFe	16.6	2.0	2.2	11.0	20.7	9.7	13.9	6.5	47
1980	PMn	0.62	0.08	0.19	1.84	0.89	-0.95	0.60	-0.64	-
	DMn	5.32	0.40	1.26	2.14	6.98	4.84	4.68	3.25	-
	TMn	5.94	0.48	1.45	3.98	7.87	3.89	5.28	2.61	49
1978	Na	170.	-	14.	184.	184.	0.	124.	0.	0
1980	Na	261.	31.	76.	380.	368.	-12.	247.	-8.	-3
1981	Na	233.	23.	28.	227.	284.	58.	192.	39.	20
1978	H <sub>2</sub> O	8.8	-	0.8	9.6	-	-	6.4	-	-
1980	H <sub>2</sub> O	13.7	1.7	4.0	19.4	-	-	13.0	-	-
1981	H <sub>2</sub> O	8.9	1.1	1.2	11.0	-	-	7.5	-	-

concentrations higher than would be expected in the absence of organic matter. High concentrations of Fe (and Mn) in the sediments are enhanced by the low export of particulates from the watershed, and Fe and Mn in these sediments are relatively undiluted by other material.

The Toolik Lake budget information for all years is summarized for P, Mn, Fe and Na in Table 2-8. The budget calculation involves several major assumptions:

1. Evaporation and direct precipitation may be neglected in the water balance. According to Hobbie (1973), roughly  $5 \text{ cm yr}^{-1}$  of evaporation occurs in arctic lakes. Approximately  $20 \text{ cm yr}^{-1}$  of precipitation falls on the Toolik region, and an amount of water equivalent to between 640 and 1300  $\text{cm yr}^{-1}$  flows into the lake from streams during the thaw season.
2. The difference between lake outflow and gauged stream inflow represents a water source of unknown composition. It is assumed that this unknown source has a composition similar to the average concentration of gauged inlet streams. This may underestimate the input of particulate materials somewhat.

The data show variable inputs, outputs and lake retention rates for most elements. In 1980, a larger input of water from the watershed resulted in the highest yearly input rates for all elements studied. Incomplete measurement of spring flow in 1978 and 1981 is one reason for this difference, but it is still probable that 1980 is a higher flow year. Manganese in 1980 and TFe in 1980 and 1981 have extremely high retention rates. The predicted sedimentation of Mn, Fe

and P from the mass balance must be increased somewhat to include atmospheric inputs of these elements. A rough estimate of the size of the direct input of these elements to the lake surface is given in Table 2-9. This extra input increases the predicted 1980 sedimentation rates by only 8% for P, 1.5% for Mn and 4% for Fe.

Because of the incomplete early season data in 1978 and 1981, 1980 is the only year for which meaningful mass balances can be calculated for Toolik Lake. The other years are useful for comparing the size of some of the mass terms, but not for a detailed look at lake retention of elements.

There is a net influx of the dissolved forms of Mn and P, and a net output of the particulate forms. Water column processes are causing this important transfer from the dissolved to the particulate state for P and Mn, and to a lesser degree, for Fe. Of particular interest is the transfer of P from the dissolved to the particulate state. The net rate of transfer may be estimated from the sum of the TDP retention rate plus the PP loss rate (Table 2-8), assuming that P is retained by the lake mainly in particulate form. This rate is  $1.37 \text{ mmol m}^{-2} \text{ yr}^{-1}$ , equivalent to 42% of the incoming TDP.

For algal production, the most useful form of P is as inorganic phosphate (Wetzel, 1975) and it seems likely that the incorporation of P into the particulate phase involves inorganic reactive P. From the 1978 inflow and outflow data, it is estimated that 40% of the incoming TDP is reactive, with equivalent amounts entering and leaving the lake. A portion of "unreactive" P must be mineralized to reactive P

Table 2-9. Atmospheric fluxes. It is assumed that 10 cm rain and 10 cm snow fall on Toolik Lake each year.

Element	Form	Concentration(uM)	Flux( $\text{mmol m}^{-2} \text{yr}^{-1}$ )
P	snow	0.56	0.06
	rain	0.33	0.03
Mn	snow	0.4	0.04
Fe	snow	5.0	0.5

Table 2-10. 1981 sediment trap fluxes. The net water column sedimentation value is from the stream budget plus the atmospheric flux. Two traps were used ("A" and "B"). All flux rates are in  $\text{mmol m}^{-2} \text{yr}^{-1}$ .

Element	A	B	mean	SD	1980 net
P	1.15	1.31	1.23	0.08	1.24
Mn	2.30	2.35	2.32	0.03	2.65
Fe	16.9	16.5	16.7	0.2	13.1

in order to include it in algal biomass. A mineralization rate of  $1.4 \text{ mmol m}^{-2} \text{ yr}^{-1}$  of unreactive P may be calculated. Using the average molar C:P ratio for lake phytoplankton of 103:1 (Vallentyne, 1973) or the mean particulate C:P ratio of the top 5 m of water column on 1 July 1980, a value of 340:1, the P requirement for water column production is between  $3.4$  and  $11.3 \text{ mmol m}^{-2} \text{ yr}^{-1}$ . This assumes a water column primary production of  $14 \text{ g C m}^{-2} \text{ yr}^{-1}$  (M.C. Miller et al., unpublished manuscript). The biologically active P must minimally cycle through the phytoplankton between 2.4 and 8 times each year.

Mineralization of unreactive P species and stream inputs of reactive P may strongly influence the productivity of Toolik Lake. Similarly, the conversion of dissolved organic N to forms usable for primary production may be an important part of the N cycle in Toolik Lake (S. Whalen, unpublished data).

The sediment trap data are useful for comparing flux estimates of Mn, Fe and P by two different methods; watershed mass balance and direct estimates. Table 2-10 presents the 1981 sediment trap flux rates and the 1980 net retention rates from a mass balance. The sediment trap data are somewhat incomplete; particulates settle out of the water column in the fall and summer, and samples from the period in which ice-out occurred were not collected. The agreement of the two rates, although taken in two different years, confirm that the estimated retention rates of P, Mn and Fe are reasonable.

### STREAM AND WATER COLUMN CONCLUSIONS

This study of lake and stream processes has produced some new observations and hypotheses about the geochemistry of Mn, Fe and P in arctic foothill lakes. These are:

1. The influxes of solutes and particulates to Toolik Lake have distinct seasonal patterns, with higher concentrations of many solutes and particulates (especially TDP, TFe, DFe and DMn) occurring during the first 7 to 10 days of the summer flow season.
2. Mineralization of dissolved unreactive P is an important part of the P cycle, and may represent one key to understanding lake productivity.
3. The removal of Mn and Fe from the water column of Toolik Lake may result from biological processes.
4. Sediment traps and stream mass balances predict similar rates of Mn, Fe and P retention by the lake.
5. Watershed export rates of solutes are extremely low, especially for Na, K, Ca and Mg, and these cation export rates are the lowest on record. Low rates of weathering are responsible.

A more general description of the cycles of Fe, Mn and P, including a budget for the sediment cycle of these elements is presented in Chapter 7. Lead-210 derived sedimentation rates for Mn, Fe and P will be compared with rates determined in this chapter.

### CHAPTER 3. SOLID PHASE CHEMISTRY OF MANGANESE, IRON AND PHOSPHORUS

The purpose of this chapter is to describe the geochemical distribution of Mn, Fe, P, Al, organic matter, pH and pE in Toolik Lake sediment, and to discuss the features of this sediment environment which result in heterogeneous distributions of major sediment components. The distribution of Mn, Fe and P in lake sediments is often controlled by redox reactions which can concentrate these elements in oxidized zones (Robbins and Callender, 1975; Carignan and Flett, 1981; Tessenow and Baynes, 1975) and result in the formation of Mn(II) and Fe(II) phosphates, carbonates or sulfides (Tessenow, 1974; Emerson and Widmer, 1978; Cook, 1981).

Toolik Lake has oxic conditions in the water column and in much of the surficial sediment, forming a barrier to the diffusion of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{PO}_4$  out of sediments and into the water column, and resulting in the formation of Mn, Fe and P enriched zones. The roles of diagenetic and depositional processes will be addressed in a descriptive manner here.

#### METHODS

A KB corer was used to obtain 5.0 cm diameter cores and metal tubing was used to push 7.5 cm diameter plastic core liners into near-shore sediments. Both coring methods resulted in relatively undisturbed cores 25 to 45 cm in length. Some surficial samples were obtained using an Ekman dredge.

Both pE and pH were determined by direct insertion of combination electrodes into fresh cores. Cores were sectioned into 1.0 to 5.0 cm thick segments, placed in plastic bags and kept frozen until further analysis. Sediment was dried overnight at 65°C and homogenized with a ceramic mortar and pestle. Organic matter content was estimated by weight loss after ignition at 500°C.

A  $\text{LiBO}_2$  fusion technique (Medlin et al., 1969) was used to put sediment components into solution. Oxalate-extractable metals and P were obtained from wet sediment by the extraction technique of Williams et al. (1971). Atomic absorption spectrophotometry was used to determine Mn, Fe and Al concentrations in both fusion and oxalate extraction solutions (Raad et al., 1969). Phosphorus was determined by the molybdate blue method (Strickland and Parsons, 1965).

The coefficients of variation of the fusion and extraction analyses were generally better than 5% for all parameters. It should be noted that the term surficial sediment refers to the top 1.0 cm of sediment.



## RESULTS AND DISCUSSION

The sediment samples examined in this study came from a wide variety of depositional environments (Figure 3-1). Sediment from near the lake's two major inlets was coarse grained with leaf material from terrestrial runoff. In the littoral zone, the sediment-water interface usually was covered with an orange Fe floc, often coating aquatic mosses and Nitella. Profundal zone sediments have a distinct Mn crust on or just below the sediment surface, extending down to 6.0 cm in some locations. An Fe crust is often found immediately below the Mn crust, typically having a thickness of less than 1.0 cm. The porosity of these crusts is always greater than 95%, and Pb-210 data (Chapter 4) indicate that these crusts are located within accumulating sediment.

### Surficial Sediment

Table 3-1 presents the range of values of surficial chemistry found in this study. Total and oxalate-extractable Mn have the largest coefficients of variation, and organic matter and total Al have the least.

Organic matter concentrations are typically between 150 and 250 mg g<sup>-1</sup>, averaging 186 mg g<sup>-1</sup>. An organic matter to organic carbon ratio of 2:1, determined using samples analyzed with a total carbon analyzer, indicates that surficial samples include 9 ± 2% organic C. The carbon budget of this system is dominated by terrestrial inputs and the input of this refractory organic matter, combined with slow

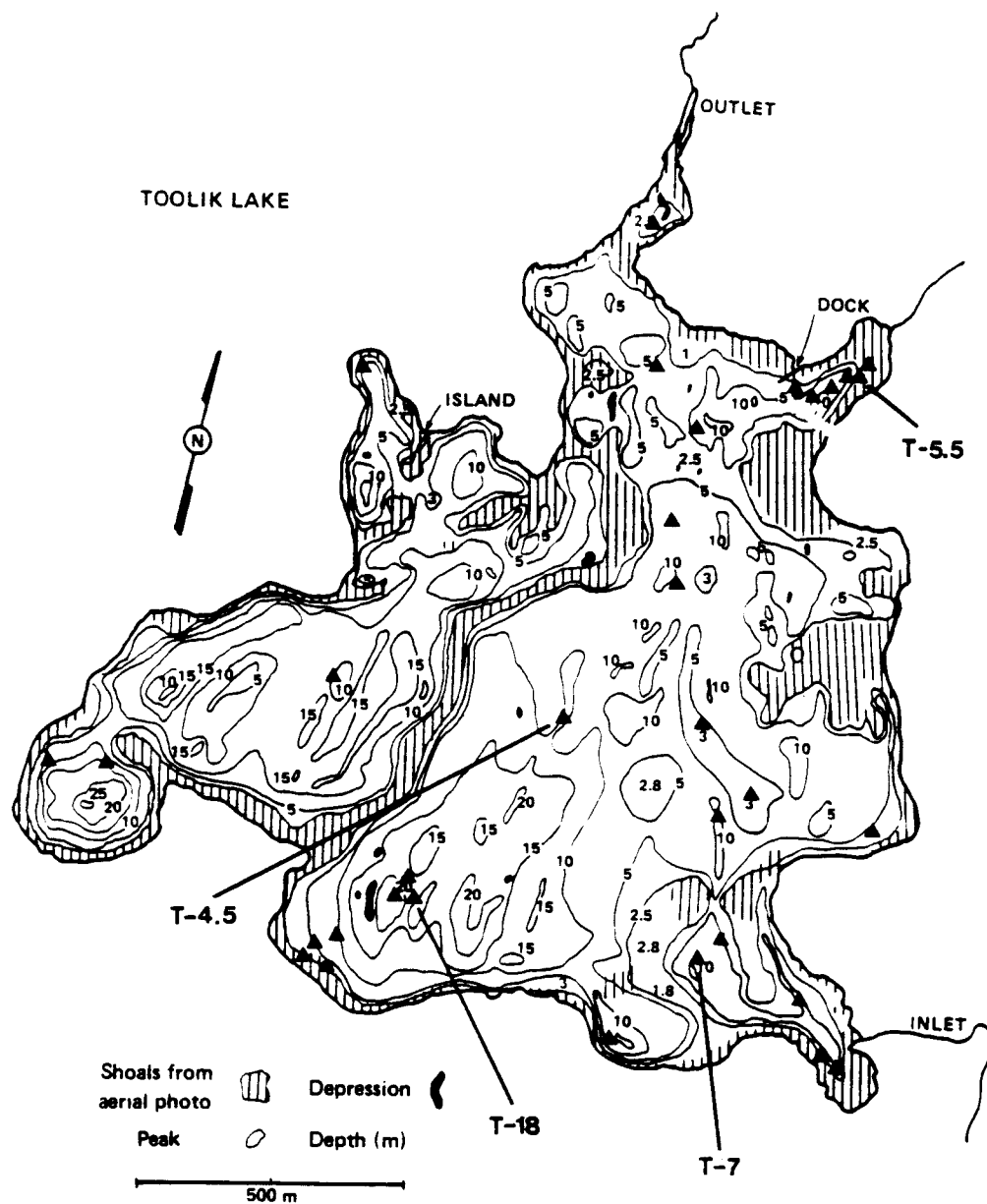


Figure 3-1. Map of Toolik Lake showing location of four cores (labelled with sampling depths). The other marked sites are surficial sediment locations.

Table 3-1. Surficial sediment chemical minima, maxima and statistics.  
 All values are in milligram per gram of dry sediment.  
 Oxalate Mn was not measured on the sample with the highest  
 total Mn.

	Minimum	Maximum	Median	Mean	Standard Deviation	Number Analyzed
Organic	75	287	186	187	43	34
Total Al	29	68	44	45	7	34
Oxalate Al	1.2	7.6	3.4	3.4	1.3	31
Total P	0.86	4.09	1.78	1.84	0.67	34
Oxalate P	0.10	2.06	0.71	0.76	0.52	31
Total Fe	17	177	74	78	48	34
Oxalate Fe	6	149	53	56	44	31
Total Mn	0.3	167	2.8	25	36	34
Oxalate Mn	0.1	91	1.0	15.7	26	25

rates of decomposition and low inputs of inorganic minerals, make the high organic content seem reasonable. Although the organic content is high, slow sedimentation rates result in relatively low rates of organic matter deposition.

Organic matter is not significantly correlated ( $p < 0.01$ ) with any other surficial sediment parameter, but the highest concentrations of organic matter are found in the littoral zone (Figure 3-2a). These higher concentrations result from epibenthic diatoms, mosses and Nitella. Inputs of detritus from Carex, an aquatic sedge, may be an important carbon source for nearshore sediments (Federle, 1981).

Total Al averages less than 5% of total sediment and varies relatively little in these sediments. Its distribution is not significantly correlated ( $p < 0.01$ ) with any parameter except oxalate Al, a measure of amorphous Al. Oxalate Al is positively correlated with overlying water depth, perhaps reflecting a grain size difference in which Al bearing minerals have more oxalate-extractable Al because of an increased surface to volume ratio. No grain size data are available to test this hypothesis.

High concentrations of Mn are found in most surficial profundal sediments (Figure 3-2b). Littoral zone sediments generally have less than 1% Mn content and profundal sediments have up to 17% Mn. Sediments with Mn concentrations above 7 or 8% usually have dark brown or black crusts in which the sediment is cemented together with Mn oxides. Observations of Mn crusts with a scanning electron microscope confirm this; diatom tests are cemented together with Mn oxides.

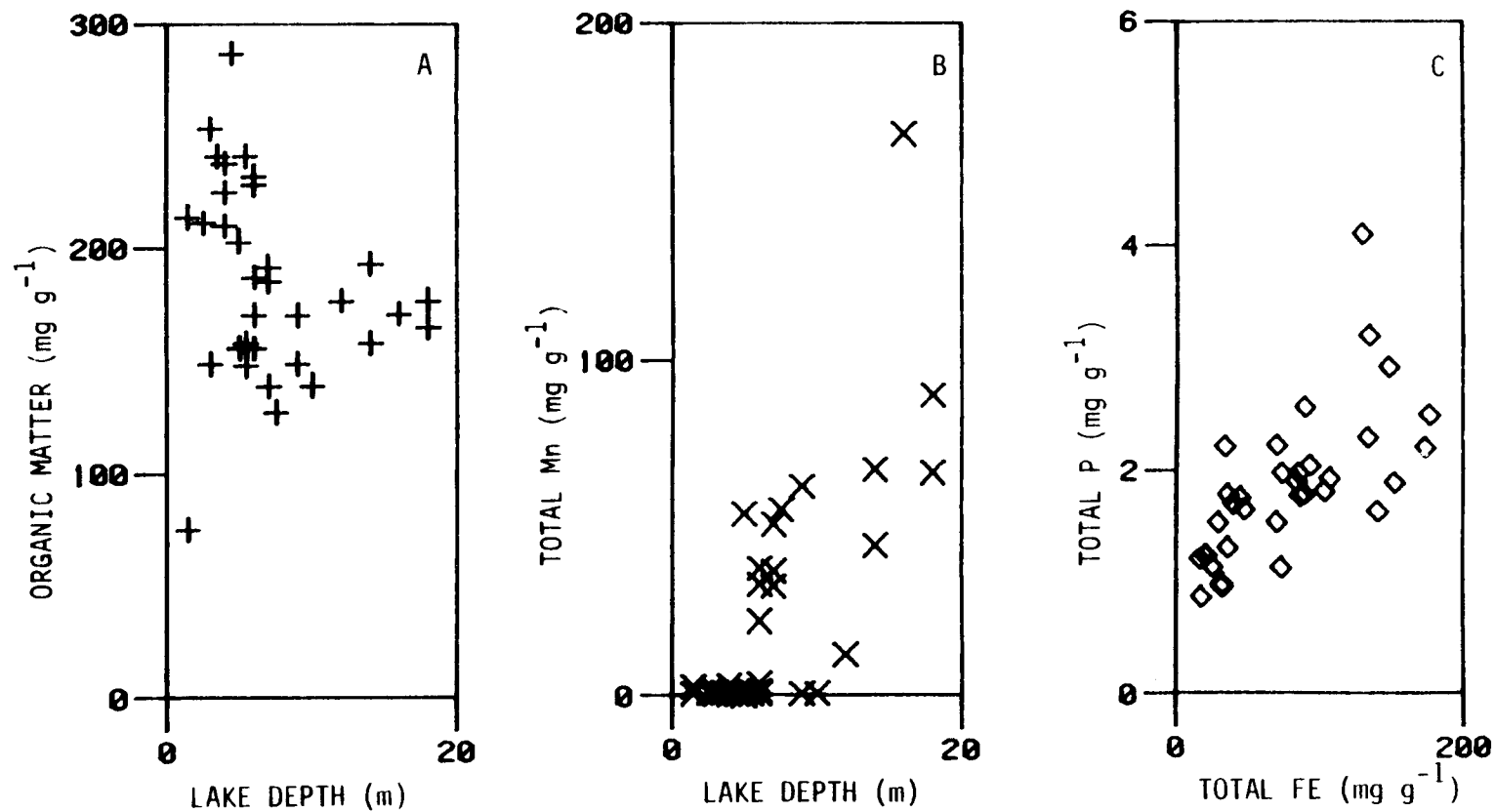


Figure 3-2. Surficial chemistry showing: a. Organic matter content as a function of water depth; b. total Mn content as a function of water depth; c. total P as a function of total Fe.

Concentrations of oxalate extractable and total surficial Mn are virtually identical, indicating the existence of relatively labile forms of Mn in these sediments. Increased Mn content in profundal zone sediments may result from increased sedimentation of Mn containing particles at greater lake depths or diagenetic loss of Mn from littoral sediment via  $\text{Mn}^{2+}$  diffusion.

The concentration of total Fe is high in most surficial sediments, averaging between 7 and 8% of total sediment (Table 3-1). Although the oxalate extractable percentage of total Fe is less than the equivalent Mn percentage, on the average over 70% is extractable. In surficial sediments, Fe as Fe(III) hydroxide could constitute over one third of the sediment mass. The highest surficial Fe concentrations are found at water depths greater than 5 m, although high variability occurs in Fe content at all depths. Total Fe is correlated only with oxalate Fe, total P and oxalate P.

Total P in these surficial sediments averages  $1.8 \text{ mg g}^{-1}$  with some values as high as  $4.1 \text{ mg g}^{-1}$ . The proportion of total P which is oxalate-extractable is highly variable, ranging from 0.12 to 0.94. Seventy-seven percent of the samples had oxalate to total P ratios less than 0.5. A correlation between P and Fe content has been found in numerous lake studies (Delfino *et al.*, 1969; Williams *et al.*, 1971; Bortleson and Lee, 1972; and others) and is generally attributed to sorption processes. The Fe-P relationship shows some scatter (Figure 3-1c), but Fe and P are significantly correlated (Table 3-2). No other measured sediment parameters are correlated with either total P

Table 3-2. Molar ratios and correlation coefficients for total Fe:P, total Mn:P and total Fe:Mn in four cores and surficial sediments. Data from within Mn crusts (T-18 and T-7) and Fe crusts (T-18) are not included in ratios or correlation coefficients, and ratios involving Mn in surficial sediments were not included because of extremely high variability in Mn content. The number of samples which form the basis of the correlation coefficient are included in parentheses and asterisks indicate correlations significant at the 99% confidence level.

Parameter		CORE ID				
		T-18	T-7	T-5.5	T-4.5	Surface
Total Fe:Total P	- ratio	22 ± 2	24 ± 5	19 ± 4	11 ± 2	23 ± 11
	- r	0.949 (9)*	0.940 (6)*	0.949 (11)*	0.176 (8)	0.672 (34)*
Oxalate Fe:Oxalate P	- ratio	22 ± 2	---	41 ± 14	9 ± 1	44 ± 26
	- r	0.915 (9)*	---	0.855 (11)*	0.633 (8)	0.701 (31)*
Total Mn:Total P	- ratio	0.9 ± 0.1	1.9 ± 1.3	0.2 ± 0.1	0.2 ± 0.1	---
	- r	0.988 (9)*	0.354 (6)	0.801 (11)*	0.962 (8)*	---
Total Fe:Total Mn	- ratio	25 ± 4	23 ± 6	114 ± 44	68 ± 5	---
	- r	0.934 (9)*	0.506 (6)	0.943 (11)*	-0.224 (8)	---

or oxalate P. Vertical distributions of P in cores will be used in the next section to examine the nature of the Fe-P association.

#### Vertical Distribution of Manganese and Iron

The data from the four cores which are presented in this chapter are found in figures 3-3, 3-4, 3-5 and 3-6. The core identification includes the depth of water from which the cores were obtained, and locations are indicated in Figure 3-1. The sediment surface of T-4.5 was covered with Nitella. Organic matter in these cores generally decreased with depth to values 20 to 40% less than surficial values. A consequence of the oxidation of organic matter is a shift towards more reducing conditions. Large decreases in pE are found in cores T-18 and T-7, a lesser change is seen in T-5.5, and T-4.5 shows little change throughout.

In core T-18, large changes in total Mn and Fe concentrations were found. A Mn crust 3 cm thick was found, with a 0.5 cm thick Fe crust immediately beneath. The Mn crust has pE values 3 units higher than the Fe crust, indicating a strong change in redox conditions at the junction of the two crusts. Reducing conditions beneath the Mn and Fe crusts suggest that  $Mn^{2+}$  and  $Fe^{2+}$  production occurs beneath these crusts.

The formation of metal oxide crusts can be explained by examining the sequence of electron acceptors used in the oxidation of organic matter (Table 3-3). Near the sediment-water interface, microbial organic matter oxidation uses dissolved oxygen as the primary oxidant.



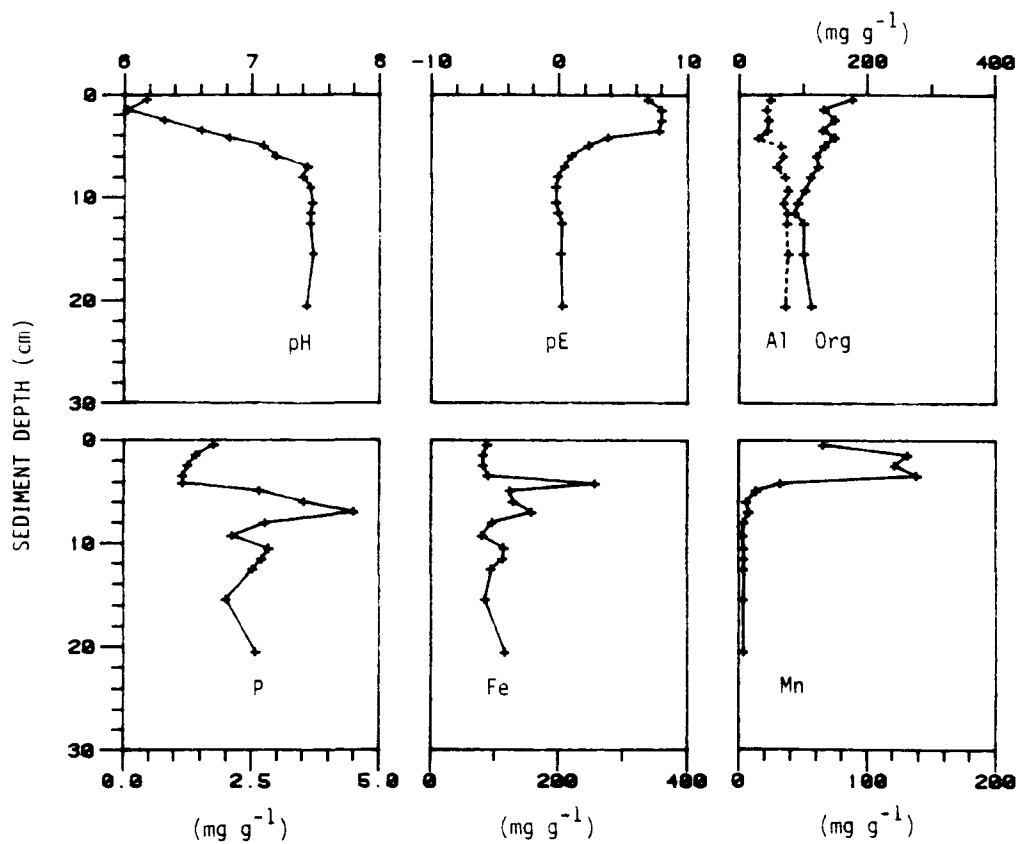


Figure 3-3. Core T-18 chemistry. The core was collected in 1979 from 18 m depth in the lake's main basin. High concentrations of Mn and Fe take the form of crusts which cement sediment particles together.

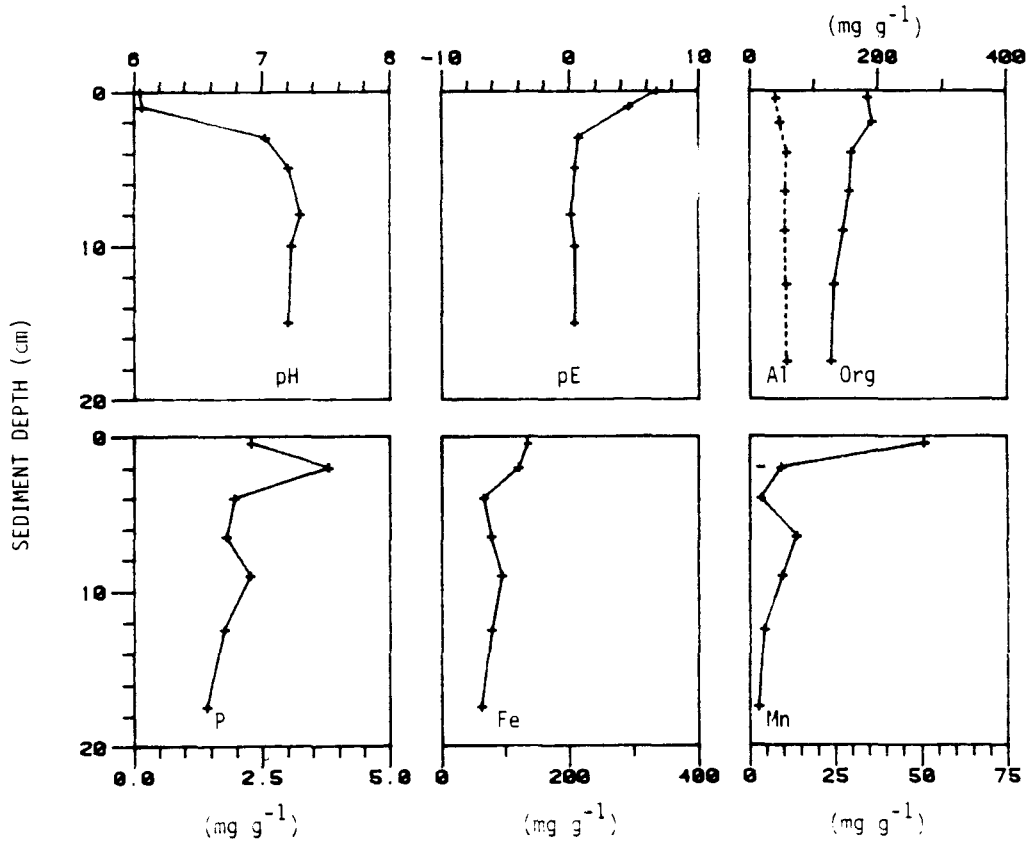


Figure 3-4. Core T-7 chemistry. The core was collected in 1978 from 7 m depth in the southeast side of the lake.

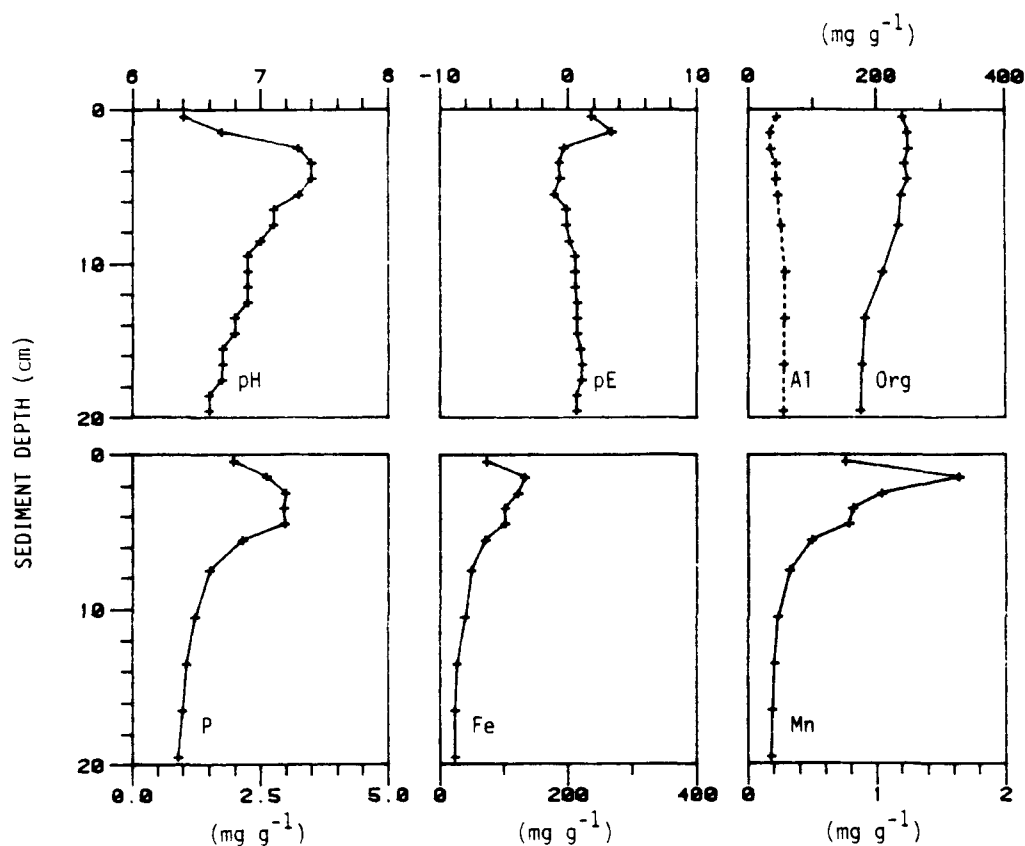


Figure 3-5. Core T-5.5 chemistry. The core was collected in 1979 from 5.5 m depth near the lake's secondary inlet. The sediment surface was covered with an orange floc. Note the Mn scale change from the previous figures.

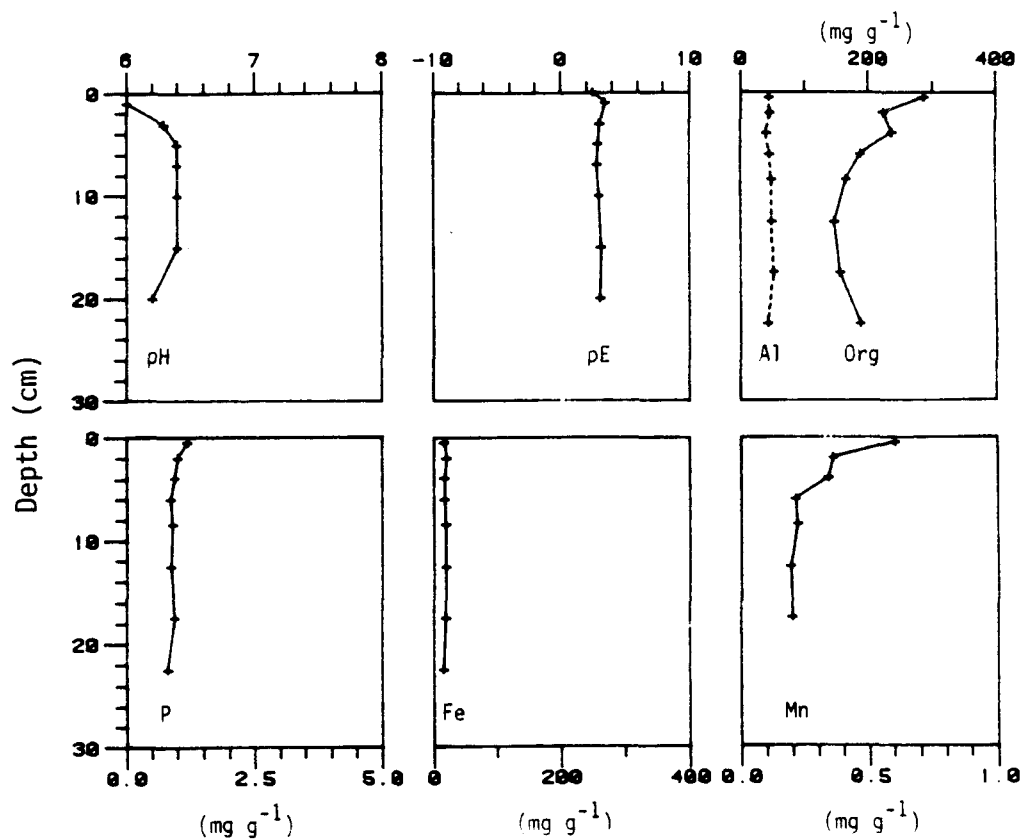
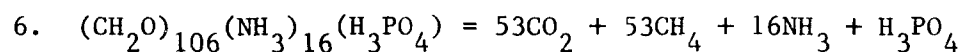
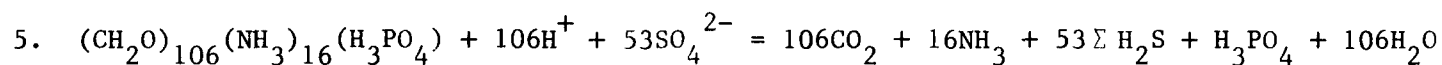
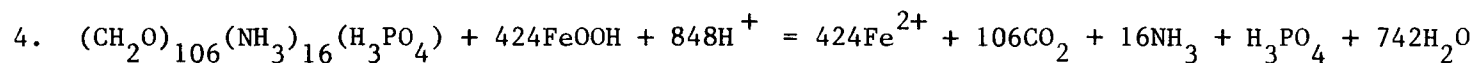
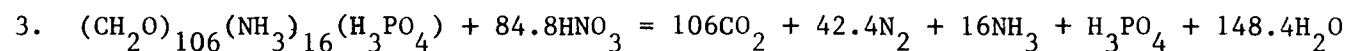
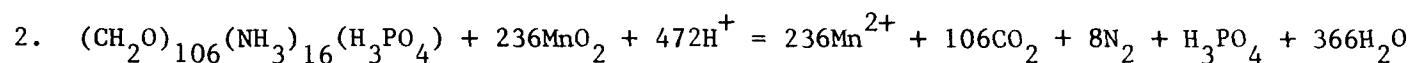
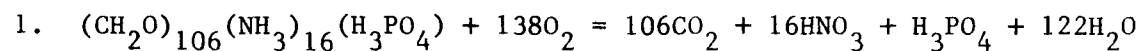


Figure 3-6. Core T-4.5 chemistry. The core was collected in 1978 from the middle of the lake. Nitella covered the sediment surface.

Table 3-3. Oxidative reactions for organic material of the Redfield composition (equations from Froelich et al. 1979).



Rates of denitrification and nitrate reduction are slow in this system because of extremely low concentrations of interstitial nitrate (Klingensmith, 1981). After most of the oxygen has been depleted, reduction of Mn(IV) oxide occurs. When the Mn(IV) has been depleted, reduction of Fe(III) oxides and hydroxides proceeds until most of the Fe(III) is consumed and sulfate reduction proceeds. This last reaction may not occur in Toolik Lake sediment because of an excess of Fe(III) over that necessary for organic matter oxidation. This lack of importance of sulfide production is an important feature of these lake sediments because formation of iron sulfides would tend to bury more Fe as Fe(II) and eventually limit the size of Fe oxide crusts. Positive values of pE indicate that redox conditions in these sediments are not consistent with sulfate reduction. If these crusts are steady state features of the lake bottom, the bottom side of the crusts must dissolve and  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  must diffuse upward to a more oxidizing zone where oxides or hydroxides are precipitated. This same mechanism concentrates Mn and Fe in oxidized zones in other sedimentary environments (Robbins and Callender, 1975; Tessenow and Baynes, 1975; Froelich *et al.*, 1979). Further evidence for the viability of this mechanism of crust formation can be found by examining the effect of metal dissolution and precipitation on pH in sediment profiles (Table 3-3). The reduction of one mole of Mn(IV) oxide or Fe(III) hydroxide consumes 1.54 or 1.75 moles  $\text{H}^+$  respectively (taking  $\text{CO}_2$  to  $\text{HCO}_3^-$ ,  $\text{NH}_3$  to  $\text{NH}_4^+$  and  $\text{H}_3\text{PO}_4$  to  $\text{HPO}_4^{2-}$ ), and a pH increase is expected.

A large increase in pH is found at the base of the crusts (Figure 3-3), indicating that metal dissolution is occurring. In the upper, more oxygenated part of the core, organic matter oxidation to bicarbonate yields protons and the oxidation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  consumes  $\text{OH}^-$ , causing the observed pH decrease of 0.6 to 0.8 (relative to the water column). The pH profile is thus consistent with a reduction/diffusion/oxidation mode of crust formation.

The separation of the Mn and Fe enriched layers in T-18 and other cores from Toolik Lake (Appendices B, D and E) is readily apparent from both visual observation and chemical analysis and is a result of the differing thermodynamic properties of the two metals (Krauskopf, 1957). Manganese oxides are stable above pE's of 0 to 2 (using equations from Stumm and Morgan, 1981). This is in general agreement with the pH, pE, Mn and Fe data from Toolik Lake (Figure 3-3). Ferrous Fe which is diffusing upward is rapidly oxidized at the bottom of the Mn crust. Oxidation of  $\text{Mn}^{2+}$  occurs much closer to the sediment-water interface, under oxic conditions. Slow rates of sediment burial are important for the almost complete separation of these two metals because upward diffusion of reduced metal to an oxidized redox horizon should balance the downward burial of Mn and Fe oxides.

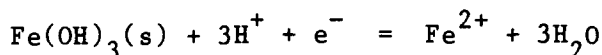
Oxalate extractions of Fe and Mn show that crusts and underlying sediments have large proportions of poorly crystallized metal oxides. Virtually all of the non-crust Mn in T-18 is extractable, while only 47% of the total Mn in the crust is oxalate-extractable. Extraction of the Mn crust with hydroxylamine hydrochloride, a strong reducing

agent, recovers virtually all of the Mn in the sediment. Oxalate extractable Fe averaged 67% of total Fe throughout the core and 80% within the crust. Most of the Fe in this core is non-crystalline and probably can participate in the redox reactions discussed previously. The high extractability of metals within this core and in surficial sediments is a key factor in the remobilization of Mn, Fe and P in early diagenesis. This is consistent with the observation that much of the Mn and Fe in the sediments is introduced into Toolik Lake in dissolved form (Chapter 2).

The distributions of Mn and Fe in T-4.5 (Figure 3-4), T-5.5 (Figure 3-5) and T-7 (Figure 3-6) may also occur from post-depositional migration. Oxidizing conditions at the sediment-water interface are necessary for the formation of Mn and Fe enriched sediments. These conditions are clearly found in T-18 and T-7, in which Mn and Fe have substantial enrichments. Cores T-5.5 and T-4.5 both are more reducing at the sediment-water interface and are depleted in Mn relative to cores from the profundal zone. Core T-4.5 has no Fe enrichments and T-5.5 has a substantial peak in Fe content at 1.5 cm.

High concentrations of sediment Fe throughout these cores (except T-4.5) suggest that Fe may play an important role in the buffering of redox conditions within these sediments. Until the Fe(III) is almost completely dissolved, it is unlikely that an energetically less favored electron acceptor such as sulfate would be utilized in the oxidation of organic matter. The following half reaction would then control pE in these sediments:





This reaction involves the exchange of 3 protons and one electron, and the following equilibrium expression may be formulated (Stumm and Morgan, 1981):

$$\text{pE} = 17.1 + \log([\text{Fe(OH)}_3]/[\text{Fe}^{2+}]) - 3\text{pH}$$

Assuming unit activity for the solid phase and rearranging:

$$\text{pE} + 3\text{pH} = 17.1 + \text{pFe}^{2+}$$

In Figure 3-7, the parameter (pE + 3pH) is plotted versus depth for all four cores, yielding values ranging from 20.5 to 22.5 in the lower parts of these cores. This would correspond to  $\text{Fe}^{2+}$  concentrations of 4 to 400  $\mu\text{M}$ , concentrations commonly found in lake sediments and similar to values found in this study (Chapter 5). Iron oxyhydroxides can strongly influence the redox environment in these cores. Except for T-18, relatively constant values of (pE + 3pH) are found below 4.0 cm.

Well documented problems with electrode response, mixed potentials and Pt-solute reactions (Stumm and Morgan, 1981) preclude the use of Pt electrode potentials for the direct estimation of  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$ . Furthermore, a lack of knowledge about the nature of Fe and Mn oxide minerals in this environment makes the choice of suitable thermodynamic constants difficult. Errors in the estimation of (pE + 3pH) could be as high as 1.0 units. Despite these problems, the coincidence of measured redox conditions in Toolik Lake sediment with that expected for  $\text{Fe(OH)}_3(\text{s})\text{-Fe}^{2+}$  equilibrium indicates that Fe plays an important role in buffering pE. These data are consistent with Fe

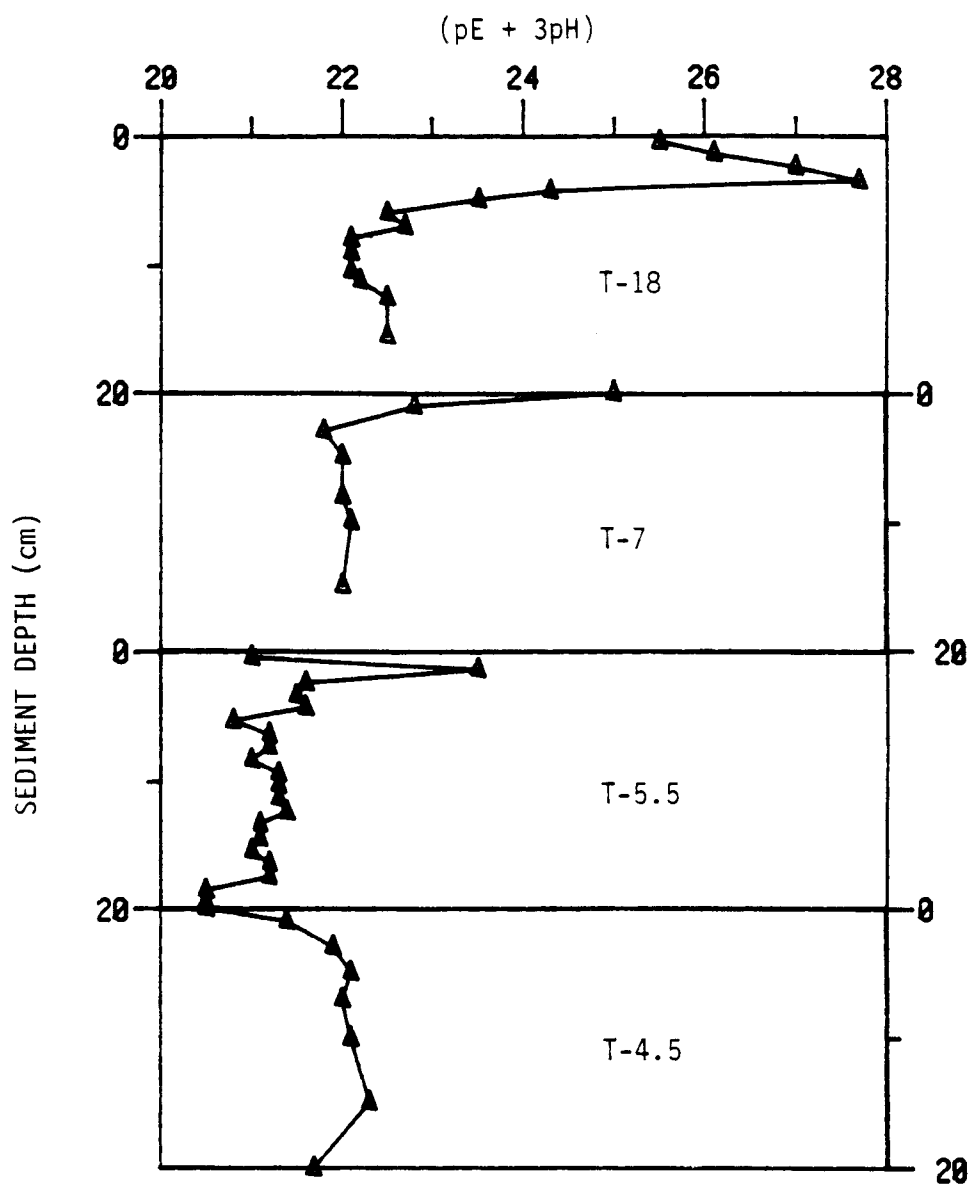


Figure 3-7. The redox parameter  $(pE + 3pH)$  plotted as a function of depth for four cores. See text for an explanation of  $(pE + 3pH)$ .

being the final electron acceptor in the upper 20 cm of these cores. The limited evidence presented here suggests that the supply of Fe(III) to the sediments is more than adequate to oxidize the metabolizable organic matter that remains after dissolved oxygen, nitrate and Mn(IV) are exhausted.

#### Vertical Distribution of Phosphorus

The P distributions in cores T-18, T-7 and T-5.5 (Figures 3-3, 3-4 and 3-5) show pronounced peaks in concentration, suggesting diagenetic redistribution (Carignan and Flett, 1981). Both T-18 and T-7 have multiple peaks in P concentration; T-5.5 has a single broad peak and T-4.5 has only a slight enrichment near the sediment-water interface. Oxalate P can be used as a measure of inorganic P (Williams *et al.*, 1971; Prentki *et al.*, 1980) and in core T-18 oxalate extraction yields P values  $84 \pm 17\%$  of those obtained from a harsher 1.0 N HCl extraction. Inorganic P varies greatly as a fraction of total P in these cores. In core T-18, oxalate P is  $27 \pm 6\%$  of total P above the P maximum and  $67 \pm 8\%$  below it. In T-5.5, the zone of highest P concentration ( $2.5 \text{ mg g}^{-1}$ ) had  $47 \pm 10\%$  oxalate P while the rest of the core has lesser amounts ( $21 \pm 4\%$ ). Oxalate P constitutes a fairly constant fraction of total P in T-4.5 ( $25 \pm 3\%$ ).

The shape of the P profiles generally matches that of Fe in these cores, especially in T-18 below the Fe crust, in T-7 except at the interface, and throughout T-5.5. Phosphorus and Fe correlate very

well in these 3 cores, but the relationship does not hold for T-4.5 (Table 3-2). In all 4 cores, the highest concentrations of total P did not correspond to the same depths as the total Fe maxima. In T-18, 2.8 cm separate Fe and P maxima, with separations of 2, 1 and 1 cm for T-7, T-5.5 and T-4.5 respectively. In all but T-4.5, the P maximum occurs below the Fe maximum.

Table 3-2 presents correlation coefficients and molar Fe:P, Fe:Mn and Mn:P ratios for the four cores. In T-18, the Mn and Fe crust sections have not been included in the correlation and in the molar ratio calculations, and the surficial section has been omitted in T-7. Total Fe and total P are significantly correlated in all cores except T-4.5, with similar results for oxalate Fe and oxalate P. Average total Fe to total P atomic ratios range from 19 to 24 for T-18, T-7 and T-5.5, but this ratio is significantly lower in T-4.5. In core T-5.5, the oxalate Fe:P atomic ratio is twice the total Fe:P ratio, with good agreement between these two ratios in both T-18 and T-4.5. The total Fe:P atomic ratio for T-18, T-7 and T-5.5 is very similar to the average total Fe:P ratio in surficial sediments (Table 3-2), although the mean surficial oxalate Fe:P ratio is similar only to that of T-5.5.

Significant Fe:Mn correlations occur only in T-18 and T-4.5, the latter being a core in which Fe and P are not correlated. Molar Mn:P ratios are very low, ranging from 0.2 to 1.9 in the four cores.

Iron-P associations in lacustrine sediments have been found in surficial sediments (Williams et al., 1971; Prentki et al., 1980; Shukla et al., 1971) and in cores (Bortleson and Lee, 1974; Carignan and Flett, 1981). Williams et al. (1971) found a strong correlation between Fe and P concentrations in sediments from 14 Wisconsin lakes and concluded that a "short order Fe-inorganic P complex" was responsible for much of the inorganic P retention in non-calcareous sediments. The Fe:P atomic ratio in their study was typically 5-10 with some samples exceeding 20, indicating a somewhat lower amount of Fe relative to P than is found in Toolik Lake surficial sediments. The oxalate Fe:P atomic ratio for surficial Toolik Lake sediments ( $44 \pm 26$ ) is several times higher than the ratio in Wisconsin lakes, similar to the Fe:inorganic P ratio of 31 found in Lake Erie (Williams et al., 1976) and considerably lower than the oxalate Fe:P atomic ratio of  $143 \pm 41$  for Barrow, Alaska pond sediments (Prentki et al., 1980). This difference between the two arctic studies (Barrow and this study) may be a result of lower amounts of P input to the Barrow aquatic ecosystem because of limited watershed size and higher retention of terrestrial P in organic form.

Sediments with lower Fe:P ratios are probably less effective in retaining phosphate in sediments, and Williams et al., (1976) have suggested that an inorganic Fe:P ratio of 7 is the minimum for effective retention of phosphate. In the four cores presented here, only T-4.5 would seem to have a possibility for P remobilization out of sediments because of the absence of significant Fe content near the

top of the core and the reducing conditions found close to the sediment-water interface. This is probably not the case for the other cores because significant Fe enrichments occur deeper in the cores (Appendix B). An absence of significant accumulations of P in Toolik Lake bottom water during winter suggests that these sediments retain all of the sedimented P.

The association of Fe, Mn and P below the oxidized interface may arise from several different processes. The Fe(III) phosphate complex may be of some importance deeper in these cores because, as hypothesized earlier, Fe(III) oxides may occur in excess of that needed to oxidize available organic matter. Emerson and Widmer (1978), Nriagu and Dell (1974), Tessenow (1974) and others have demonstrated the importance of vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) in regulating the pore water concentrations of Fe and P in reducing sediments. Tessenow (1974) has shown that mixed Fe(II)-Mn(II) phosphates are important in regulating Mn concentrations in reducing solutions. This mode of metal-phosphate association is found in Toolik Lake sediment, and Fe-Mn phosphates have been found (Chapter 5).

Low Mn:P ratios suggest that Mn does not exert significant control over P distribution in these sediments. Significant Mn-P correlations have been noted in other studies (Bortleson and Lee, 1974; Williams *et al.*, 1971), but low Mn:P ratios suggest that the correlation results from the association of both Mn and P with Fe in the sediment. The Mn concentration in the vivianite sample that was analyzed is much less than the Fe concentration, indicating that

authigenic Mn phosphate is of little importance in determining the distribution of P in reducing sediments in Toolik Lake.

The formation of distinct P enriched zones, often separate from major Fe enriched zones, represents diagenetic remobilization of P within these cores. Reducing conditions are encountered as sediment is buried and the Fe(III)-phosphate complex is dissolved as Fe(III) oxides are reduced, releasing P into solution (Krom and Berner, 1981). The same kind of dissolution/diffusion/precipitation mechanism that concentrates Mn and Fe into the oxic sediments concentrates inorganic P into distinct zones. The lack of correspondance between the highest Fe and P values in these cores may reflect a differential mobility of P relative to Fe. Phosphate may adsorb onto sediments from which Fe may be added or dissolved and  $\text{Fe}^{2+}$  may diffuse further because of lower rates of adsorption. If P sorption is the main limit on  $\text{PO}_4$  concentration near the P enriched horizon, changing surface characteristics may separate Fe and P. Changes in pH, pE or in Fe mineralogy throughout the core may alter the sorption reaction. Although the mechanism that concentrates P in some sediment zones can't be completely understood from solid phase data, it is nevertheless clear that the P enrichments are diagenetic in origin and they do not represent changes in P supply to the sediment. The importance of sediment properties to the exchange of phosphate across the sediment-water interface has been noted by Mortimer (1971) and others. Mortimer's classic experiments clearly show that anoxic conditions result in the release of  $\text{Fe}^{2+}$  and  $\text{PO}_4$  from sediment once the oxidized zone at

the sediment surface has broken down. In Toolik Lake sediment, oxidized conditions can extend 4 cm into the sediment, as in core T-18, or be extremely thin or non-existent. This P trap has important consequences for lake metabolism. The inorganic P content of the surface 0.05 cm of the lake bottom is equivalent to the entire water column content of P (average total P in the water column =  $10 \text{ ug l}^{-1}$ , mean depth of lake is 7 m, surficial sediment solids content =  $0.10 \text{ g cm}^{-3}$ , average oxalate P =  $1.78 \text{ mg g}^{-1}$ ).

Arctic lakes are extremely unproductive because of low inputs of P (de March, 1975) and they are susceptible to eutrophication from anthropogenic nutrient loading (Schindler et al., 1974b). High concentrations of Mn and Fe in Toolik Lake sediment represent a large pool of electron acceptors which must be reduced before significant phosphorus release would occur. It is likely that any short term perturbation involving increased organic loading would not significantly affect P return from sediment because of effective redox buffering by Mn and Fe.



#### DEPOSITION VERSUS DIAGENESIS: CONTROL OF SOLID PHASE CHEMISTRY

The heterogeneous distribution of Mn, Fe and P in Toolik Lake surficial sediments results from both diagenetic and depositional processes. The large differences in Mn, Fe and P concentrations within cores indicate that diagenesis has a strong effect upon the distribution of these elements.

The absence of significant concentrations of Mn in surficial sediments from the littoral zone may be a function of preferred settling of fine, Mn containing particles in greater lake depths. Another possible explanation is that the higher organic matter concentrations in the littoral zone result in reducing conditions in surficial sediments; Mn may dissolve, migrate into the water column, and eventually become incorporated into profundal sediments. An interesting question is whether the more reduced conditions found in littoral sediments are a result of greater rates of organic matter oxidation, or lower inputs of electron acceptors (Mn(IV), Fe(III)). Undoubtedly, both processes are involved, and it is clear that significant Mn accumulations occur only within oxic sediments, usually within the profundal zone.

Iron concentrations in surficial sediment are not correlated with lake depth, and Fe is less likely to be remobilized from sediments than is Mn, for both kinetic and thermodynamic reasons (Stumm and Morgan, 1981). The lack of similarity between Mn and Fe distributions in surficial sediment may also result from the occurrence of maximum Fe concentrations deep within some cores. Phosphorus concentrations

within sediments are highly correlated with Fe concentrations because of simultaneous migrations of these two elements in sediments (Carignan and Flett, 1981).

An understanding of the quantitative role of diagenetic processes in the formation of these sediments can best be accomplished by considering the various fluxes of Mn, Fe and P both within sediments and in the lake. Chapters 4 and 5, plus the water column budget data from Chapter 2 will provide the rate information necessary for a quantitative investigation of these processes.

## CHAPTER 4. LEAD-210 GEOCHRONOLOGY

The determination of sedimentation rates via the Pb-210 methodology in lakes provides information which is useful for many purposes. It has been used for estimating losses of nutrient elements to sediment (de March, 1978; Kipphut, 1978; Evans and Rigler, 1980a), inputs of trace substances of anthropogenic origin (Edgington and Robbins, 1976), rates of particle reworking processes (Kipphut, 1978; Robbins, 1978) and for the study of sediment diagenesis (Robbins and Callender, 1975; Carignan and Flett, 1981). The Pb-210 dating method is useful for dating lake sediments because the Pb-210 half life of 22.3 yr is ideal for looking at recent (<100 yr) sedimentation (Krishnaswami and Lal, 1978; Robbins, 1978).

Lead-210 dating of Toolik Lake sediments was undertaken for three purposes:

1. To investigate annual loss rates of metals and nutrients from the water column.
2. To provide information on burial rates of Mn and Fe oxides necessary for modelling of Mn and Fe migration in the sediments.
3. To evaluate the applicability of this dating method to sediments with extremely low rates of accumulation and in which Mn and Fe diagenesis greatly alters the bulk composition of the sediment.

Rates of sedimentation in arctic lakes have been estimated in one previous study (de March, 1978), and that study depended mostly on very indirect methods of sedimentation rate calculation. This study

is the first extensive application of the Pb-210 technique to arctic lake sediments.

A brief outline of the principles behind the use of Pb-210 as a geochronometer will be presented here; detailed descriptions of its application are available elsewhere (Robbins, 1978; Krishnaswami and Lal, 1978). Radon-222 gas emanates from soils as a result of the decay of soil Ra-226, and because this gas has a half-life of only 3.8 days, Pb-210 is rapidly formed after the brief appearance of several short lived intermediates. Atmospheric Pb-210 is removed by precipitation and particulates and is deposited at the lake surface, where it is rapidly removed from the water column by particles (Robbins, 1978). Lead-210 may be used as a geochronometer if the flux of Pb-210 to the sediment surface is constant and it does not migrate after deposition. It appears that both of these requirements are adequately met in most applications of the technique to lakes (Krishnaswami and Lal, 1978).

#### METHODS

Cores for Pb-210 dating were obtained from 12 sites in Toolik Lake, including a depth transect of five cores on the west side of the main basin, as well as a series of seven cores on the east side of the lake's main basin (Figure 1-2). All 1979 cores were obtained in September 1979 by subcoring an Ekman dredge with 6.6 cm inner diameter polycarbonate tubing yielding short undisturbed cores 7 to 10 cm in length. All 1980 cores were obtained in May and June 1980 through the

ice using a KB corer modified to hold 6.6 cm inner diameter core liners. The corer was slowly lowered, not dropped, into soft sediment. Undisturbed cores 20 to 45 cm in length were obtained in this manner and 1.0 cm thick sections were immediately extruded and sectioned after collection, and frozen in plastic bags until later analysis.

The percent water was determined by drying samples at 65 °C, and dried mud was homogenized with a ceramic mortar and pestle. Approximately 1.0 to 2.0 g of sediment were weighed into 250 ml borosilicate glass beakers for analysis of Po-210, a Pb-210 daughter nuclide with a 134 day half life. The sample was leached for 1.5 hr with 6.0 N HCl at 80-90 °C, with Po-208 added as a yield tracer. The sediment was removed by centrifugation, the leachate was evaporated to a volume of approximately 10 ml, and after adjusting the volume to 100 ml with distilled water, the Po was spontaneously plated on a silver plate for 1.5 hr at 80 °C. Ascorbic acid was added to the plating solution to minimize iron interferences. Counting in Ortec alpha counters was in all cases long enough to produce a counting error of less than 5%. Secular equilibrium between Po-210 and Pb-210 is assumed and all activities are referred to as Pb-210.

Total Al, Fe and Mn were determined by atomic absorption following LiBO<sub>2</sub> fusion (Medlin et al., 1969). Porosity was calculated from the percent water data assuming the density of the solid material to be 2.5 g cm<sup>-3</sup>. The Pb-210 data used in this chapter is presented in Appendix C.

### CALCULATION of SEDIMENTATION RATES

In a sediment with constant inputs of Pb-210, constant porosity, constant sedimentation rate, no post depositional migration of Pb-210 or daughter nuclides and constant inputs of supported Pb-210 from the decay of sediment Ra-226, the following equation may be used to describe the distribution of Pb-210 in sediment:

$$A(x) = A(0) * \exp(- \lambda / w * x) + A'$$

where:

$A(x)$  = activity of total Pb-210 (dpm g<sup>-1</sup>)

$A(0)$  = activity of unsupported Pb-210 at the sediment surface

$A'$  = activity of supported Pb-210

$\lambda$  = decay constant for Pb-210 (0.0311 yr<sup>-1</sup>)

$x$  = depth (cm) below the sediment-water interface

$w$  = sedimentation rate (cm yr<sup>-1</sup>)

The activity of supported Pb-210 may be estimated from the activity of Pb-210 observed deep in a core where all of the unsupported Pb-210 has decayed away, or by direct measurement of Ra-226. In this study, Ra-226 was measured in only one core, and in the other cores Pb-210 activity deep in cores was used to estimate supported Pb-210. The supported levels are quite constant in the 1980 cores (Table 4-1). Plots of  $\ln(A(x)-A')$  versus  $x$  yield  $-\lambda/w$  as the slope, from which  $w$  (cm yr<sup>-1</sup>) may be calculated.

Substantial changes in porosity occur in many cores, so a different means of sedimentation rate calculation must be used. A

Table 4-1. Toolik Lake Pb-210 sedimentation. Two different means of calculation of sedimentation rate are used: using cumulative Al and cumulative mass as depth scales. Aluminum input (Al Input) is from the cumulative Al scale as is the mass input, which was calculated on the basis of the Al concentration deep in these cores. The mass input in parentheses is from the cumulative mass basis of calculation. Top and bottom are the depth sedimentation rates at the top (0-1 cm) and bottom of cores. Surface is the surficial concentration of Pb-210, supported is the asymptotic value of Pb-210 concentration deep in the core and Pb-210 flux is the flux of Pb-210 to the sediment surface (assuming steady state inputs).

Location	Depth (m)	Al Input (mg cm <sup>-2</sup> yr <sup>-1</sup> )	Mass Input (mg cm <sup>-2</sup> yr <sup>-1</sup> )	Top (cm yr <sup>-1</sup> )	Bottom (cm yr <sup>-1</sup> )	Surface (dpm g <sup>-1</sup> )	Supported (dpm g <sup>-1</sup> )	Pb-210 Flux (dpm cm <sup>-2</sup> yr <sup>-1</sup> )
West	3.5	0.07	1.3 (2.1)	0.01	0.005	10.88	1.63	0.04
	5.5	0.16	2.7 (3.8)	0.05	0.015	14.22	2.41	0.11
	8.0	0.18	2.6 (3.2)	0.04	0.011	20.24	2.07	0.12
	13.0	0.23	2.8 (4.4)	0.035	0.015	25.08	1.95	0.15
	18.0	0.25	3.7 (5.6)	0.08	0.023	40.82	2.50	0.26
East T97A	5.5	0.34	5.7 (6.0)	0.08		13.78	1.74	0.11
C	6.0	0.47	7.3(24.0)	0.14		12.09	2.96	0.17
D	10.0	0.33	4.9 (5.3)	0.19		24.20	1.26	0.17
E	7.5	0.25	4.1 (5.2)	0.06		19.94	2.81	0.13
F	7.0	0.35	5.8 (6.9)	0.08		16.36	2.15	0.14
G	6.0	0.41	6.4 (7.5)	0.09		16.17	0.78	0.11
CB80	8.0	0.36	5.1 (5.9)	0.06	0.024	20.94	2.15	0.13
Mean		0.28	4.4 (6.7)	0.07	0.016	19.6	2.0	0.14
Standard deviation		0.11	1.8 (5.7)	0.03	0.008	8.1	0.6	0.05
Whole Lake Rate		0.18	2.7 (4.1)					0.10

cumulative mass scale can replace the depth scale and a plot of cumulative mass ( $\text{g cm}^{-2}$ ) versus unsupported Pb-210 ( $\text{dpm g}^{-1}$ ) yields sedimentation rates on a mass basis ( $\text{mg cm}^{-2} \text{yr}^{-1}$ ). A major advantage of this technique is that error in splitting exactly 1.0 cm sections does not adversely affect Pb-210 sedimentation rate measurements, if the diameter of the core is known and the total mass of each section is completely recovered.

In Toolik Lake sediments, another complication arises in the calculation of sedimentation rates. The top 10.0 cm in most cores has large amounts of solid phase Mn and Fe, often in the form of crusts. A significant proportion of the total sediment mass in the upper parts of some cores is a result of post-depositional migration of Mn and Fe, not simple depositional processes, and it is necessary to utilize some other "conservative" sediment parameter other than total mass. Figure 4-1 shows a plot of the sum of total Fe and Mn versus total Al. In all cores with non-homogeneous distributions of Fe and Mn there is a significant ( $p < 0.01$ ) negative correlation between Al concentration and the sum of these two metals, indicating that sediment Al is being diluted by Mn and Fe. A similar relationship is observed with a plot of total K, Na and Mg versus the sum of Mn and Fe. If the concentration of Al in sedimenting material is relatively constant, it may be used as a tracer of the original sedimentary material, including the phase which carries Pb-210. This requires that Pb-210 has no post-depositional mobility relative to Al. The calculation of an Al sedimentation rate is similar to the calculation of mass sedimentation



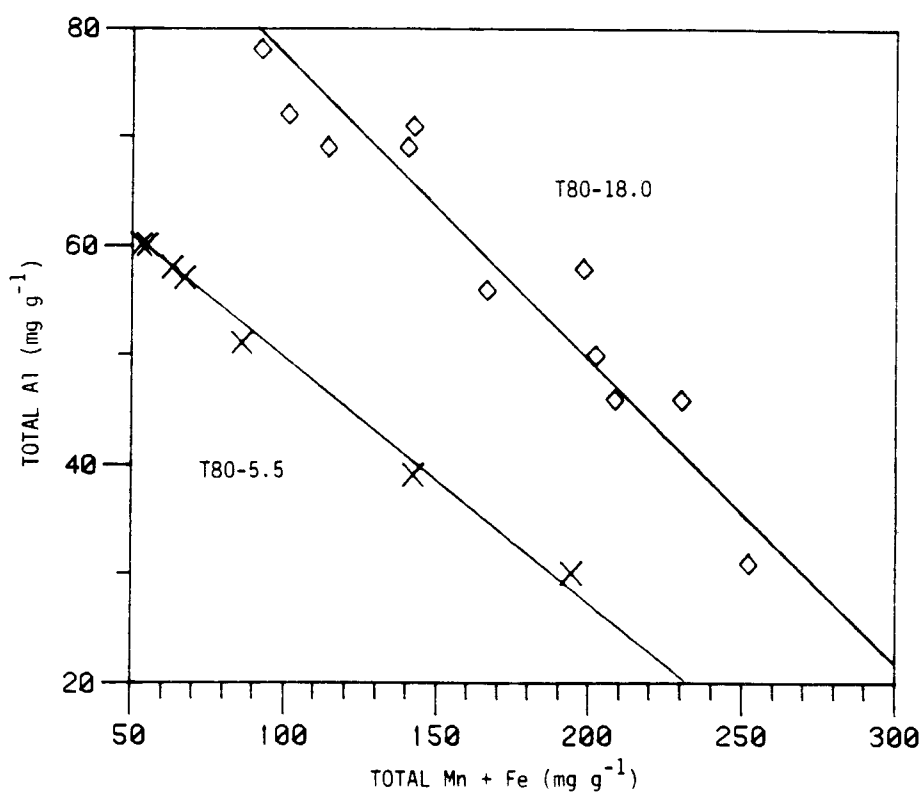


Figure 4-1. Sediment dilution by Mn and Fe oxides. The concentration of Al is negatively correlated (99% confidence) with the sum of Mn + Fe, indicating that these diagenetically formed metal rich zones are diluting sedimentary materials near the sediment-water interface.

rates, with the cumulative Al ( $\text{mg Al cm}^{-2}$ ) used as a depth scale and the concentration of Pb-210 is expressed as dpm ( $\text{mg Al}$ ) $^{-1}$ . The mass sedimentation rate ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ ) may be estimated from the mean Al content of sediment below the Mn and Fe crusts.

## RESULTS

Surficial concentrations of Pb-210 range from 10.9 to 40.8 dpm  $\text{g}^{-1}$  (Table 4-1) and are positively correlated with overlying water depth ( $r = 0.94$ ,  $n = 12$ ). Supported Pb-210 concentrations range from 1.26 to 2.96 dpm  $\text{g}^{-1}$ , averaging  $2.0 \pm 0.6$  dpm  $\text{g}^{-1}$ .

The flux of Pb-210 to sediment is very low, with inputs ranging from 0.04 to 0.26 dpm  $\text{cm}^{-2} \text{ yr}^{-1}$  and averaging  $0.14 \pm 0.05$  dpm  $\text{cm}^{-2} \text{ yr}^{-1}$ . Lead-210 flux is significantly correlated with lake depth ( $p < 0.01$ ;  $r = 0.856$ ,  $n = 12$ ) and the flux of Pb-210 to Toolik is comparable only to Char Lake, another arctic lake (Table 4-2). Figure 4-2 shows excess Pb-210 on an Al basis for four cores used in this study, with most of these cores having relatively good fits to the regression line. Core T80-3.5C had significant excess Pb-210 in only two sections, so the sedimentation rate from this site is not considered very reliable. Sedimentation rates calculated in this study ranged from 0.1 to 0.4  $\text{mg Al cm}^{-2} \text{ yr}^{-1}$  (Table 4-1; Figure 4-3). The mass sedimentation rate calculated from the Al flux ranged from 1.3 to 7.3  $\text{mg cm}^{-2} \text{ yr}^{-1}$ . Estimates of the surficial sedimentation rate vary from 0.01 to 0.14  $\text{cm yr}^{-1}$  for all 12 cores, and rates at an estimated final compaction were 0.005 to 0.024  $\text{cm yr}^{-1}$  for the T80 cores.

Table 4-2. Sedimentation rates in North American lakes.

Lake	Sedimentation Rate		Pb-210 Flux	No. of Cores	References
	(mg cm <sup>-2</sup> yr <sup>-1</sup> )	(dpm cm <sup>-2</sup> yr <sup>-1</sup> )			
Mendota	18	3.2	1	A	
Trout	60	6.4	1	A	
Tahoe	21	0.5	1	A	
Erie	83-440	-	3	B	
Huron	21-51	1.6-2.6	2	C	
Michigan	12-94	0.3-1.4	7	D	
Ontario	31-56	-	4	E	
Superior	7-83	0.2-10.0	17	F	
Bob	range	6-23	-	14	G
	whole lake	7	-	14	G
Red Chalk	whole lake	4.5	-	12	H
Costello	whole lake	4.8	-	17	H
ELA lakes	range	7-10	0.5	3	I
Char Lake	Pb-210	26	0.1	1	I
	whole lake	3.1*	-	50	J
Toolik	range	1-7	0.04-0.26	12	this study
	whole lake	2.7	0.10		

\* not using Pb-210 methodology.

#### REFERENCES

- |                                 |                                    |
|---------------------------------|------------------------------------|
| A. Koide <u>et al.</u> , 1972   | F. J.E. Evans <u>et al.</u> , 1981 |
| B. Robbins <u>et al.</u> , 1978 | G. R.D. Evans and Rigler, 1980     |
| C. Robbins <u>et al.</u> , 1977 | H. R.D. Evans and Rigler, 1983     |
| D. Robbins and Edgington, 1975  | I. Kipphut, 1978                   |
| E. Farmer, 1978                 | J. de March, 1978                  |

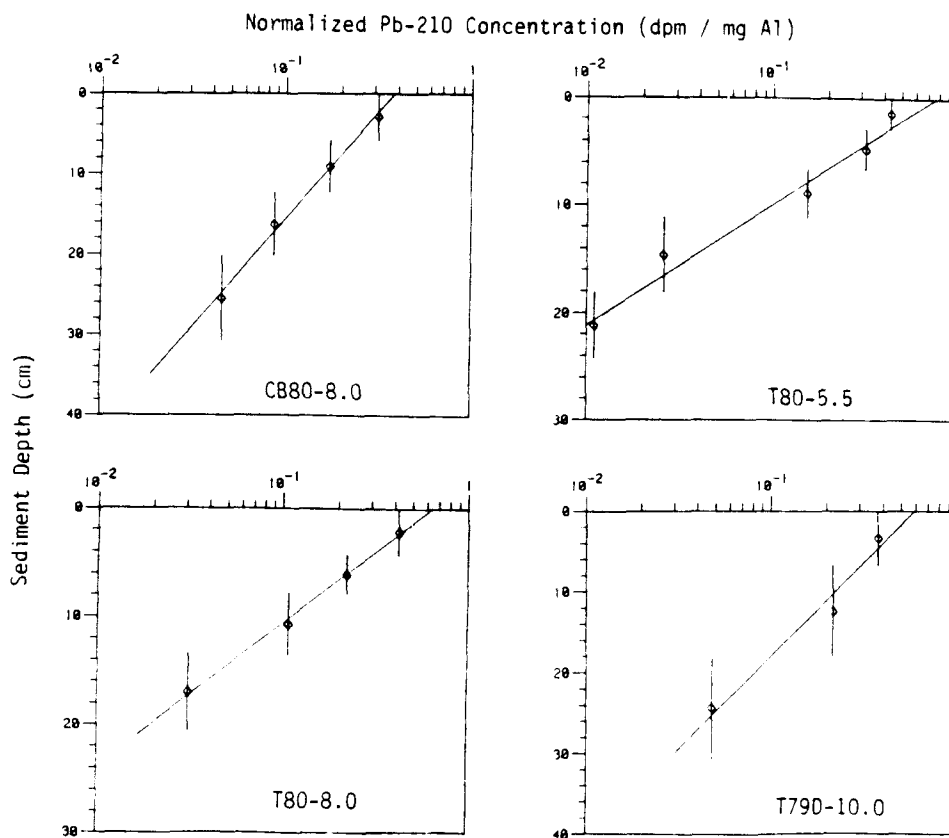


Figure 4-2. Unsupported Pb-210 concentrations (normalized to Al concentration) plotted against cumulative Al. Four of the 12 cores are shown. The lines are linear regression best fits.

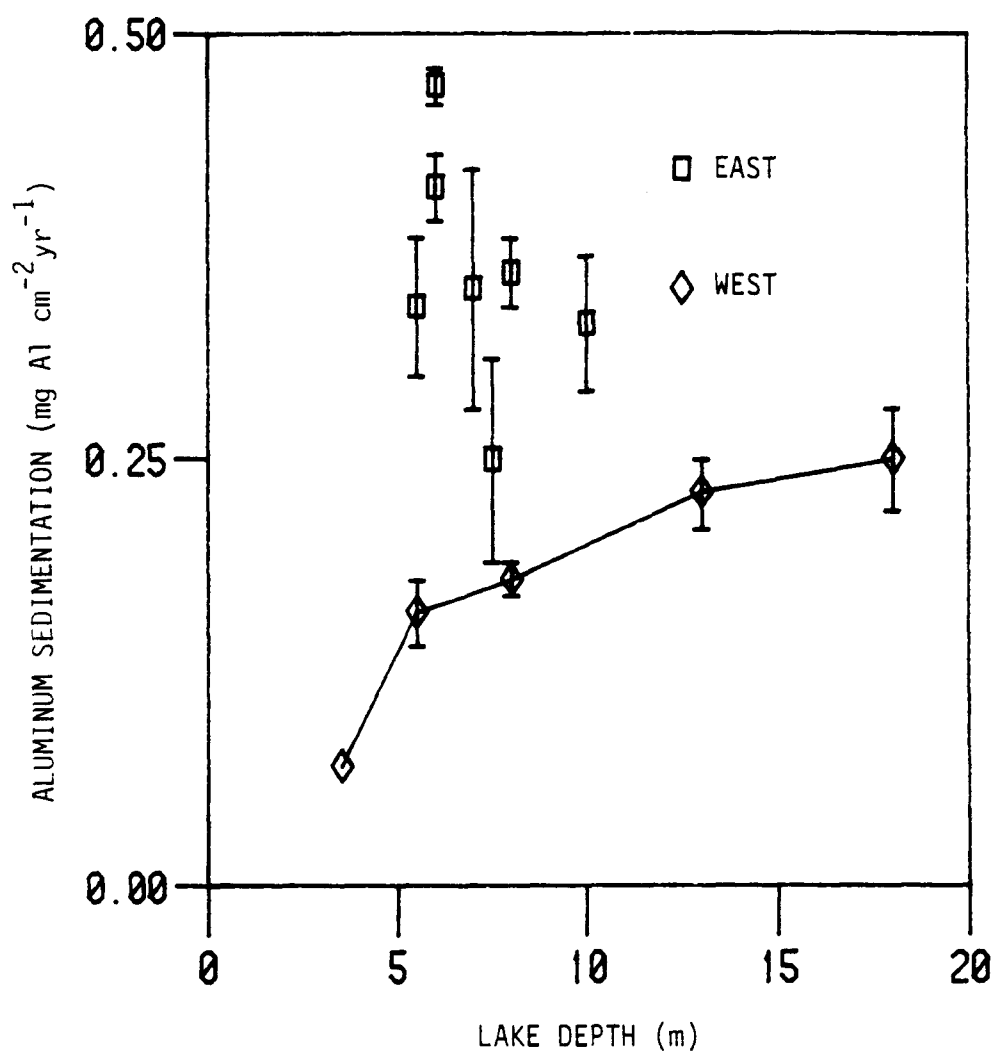


Figure 4-3. Aluminum sedimentation rates in Toolik Lake, plotted with respect to overlying water depth. Error bars represent one SE. Cores from the west transect and east side of the lake are indicated.

A whole lake rate of sediment accumulation was calculated using the following equation:

$$R = \sum_{i=1}^5 w_i F_i$$

where  $R$  is the whole lake sedimentation rate ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ ),  $w_i$  is the mean sedimentation rate in depth interval  $i$  ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ ) and  $F_i$  is the fraction of lake bottom within a given depth interval. Depth intervals were 0.0-2.5, 2.5-5.0, 5.0-10.0, 10.0-15.0 and 15.0-25.0 m. It is assumed that no sediment accumulates at water depths less than 2.5 m. The whole lake accumulation rate ( $2.7 \text{ mg cm}^{-2} \text{ yr}^{-1}$ ) is only 61% of the mean accumulation rate for all 12 cores because only 59% of the lake bottom is accumulating sediment at a appreciable rate (ie. depths > 5.0 m).

Large differences exist between mass accumulation rates calculated using the Al corrected rates and those using the simpler cumulative mass depth scale (Table 4-1). The mass scale rates are 5 to 60% higher than those estimated from the Al based method (except for T79C which was 230% higher), with a whole lake rate estimate 50% higher. These higher rates reflect the inclusion of diagenetically formed Mn and Fe oxides into the cumulative mass scale, and result in an overestimate of sediment accumulation rates.

Figure 4-4 shows the Ra-226 profile for T80-18.0D. The peak in Ra-226 activity results from diagenetic remobilization of Ra-226 associated with Mn and/or Fe oxide remobilization (Chapter 6). If this

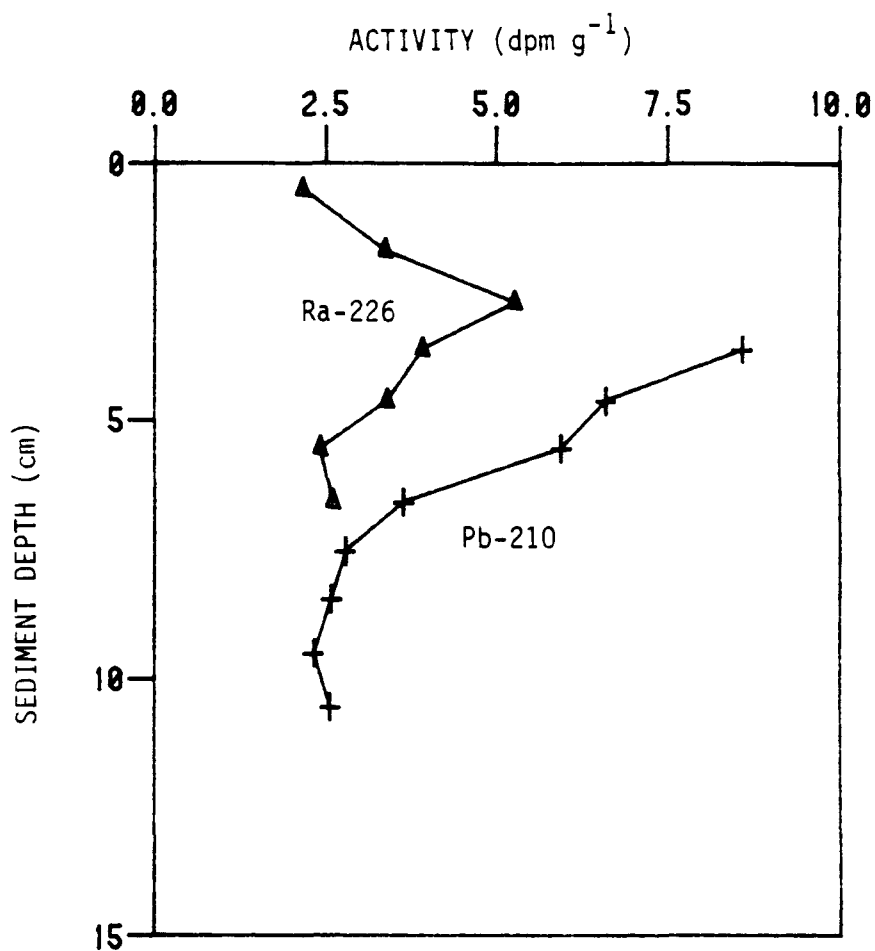


Figure 4-4. Radium-226 activity and Pb-210 data for the 18.0 m location. The peak in Ra-226 concentration corresponds with high concentrations of sediment Mn and Fe in this core.

peak is a steady state diagenetic feature, subtracting the Ra-226 from the total Pb-210 to obtain unsupported concentrations may not be correct, because equilibrium between Ra-226 and Pb-210 may not be fully attained. Diffusion of Ra-222 within sediment pore water further complicates the calculation. In the absence of further information on the diagenesis on Ra-226 and its effect on Pb-210 calculations, the Ra-226 concentrations were subtracted from the total Pb-210 concentrations to obtain unsupported concentrations. A comparison of sedimentation rates by subtraction of constant supported levels (from Pb-210 deep in the core) and section by section subtraction of Ra-226 activity was done on T80-18.0D. The two methods produce Al sedimentation rates of 0.23 and 0.25 mg Al cm<sup>-2</sup> yr<sup>-1</sup> respectively, suggesting that measurement of Ra-226 for each core is not necessary.

If the Ba content of Fe and Mn crusts may be used as an analogue for the Ra-226 content (Krishnaswami and Moore, 1973), the greatest problem in calculation of sedimentation rates should occur for T80-18.0D. Smaller changes might occur in the estimate of supported Pb-210 in several other Mn rich cores.

## DISCUSSION

Several factors are involved in the low input of Pb-210 to Toolik Lake. Low rates of precipitation and low atmospheric Pb-210 content are found at high latitudes, causing low rates of Pb-210 flux. Lower Rn-222 exhalation rates from frozen soils are also a reason for this, and the long period of snow cover each year hinders suspension of



Pb-210 containing soil and plant material into the air.

Higher rates of unsupported Pb-210 flux at greater lake depths may result from resuspension of Pb-210 containing particles from near-shore sediments. With the exception of the 3.5 m and 18.0 m locations, the fluxes fall into a small range (Table 4-1).

The concentrations of Pb-210 in surficial sediments are comparable to those found in many other lakes (Robbins, 1978). Low inputs of sediment leave the Pb-210 relatively undiluted by other material, and high porosity values have allowed adequate depth (mass) resolution for sedimentation rate calculation. If the porosity was lowered to 0.80 from the typical value of 0.95, significant amounts of supported Pb-210 would be restricted to the top 1.0 cm or less of most cores analyzed.

Toolik Lake mass sedimentation rates are extremely low, a result of the harsh climate, low rates of physical and chemical weathering, and low rates of primary production in both terrestrial and aquatic environments (Coakley and Rust, 1968). Most North American lakes accumulate sediment at much faster rates than measured for Toolik (Table 4-2). Only ELA lakes (Kipphut, 1978) and Char Lake (de March, 1978) have rates comparable to Toolik Lake. Using estimated ages of different sediment facies in 50 cores, de March (1978) calculated a mean sedimentation rate for Char Lake of  $3.1 \text{ mg cm}^{-2} \text{ yr}^{-1}$ , comparable to the estimated whole lake rate for Toolik of  $2.7 \text{ mg cm}^{-2} \text{ yr}^{-1}$ . The one Pb-210 core for Char Lake gave a rate of  $25 \text{ mg cm}^{-2} \text{ yr}^{-1}$  (de March, 1978), a value much higher than other estimates for Char Lake and

considerably higher than for any core in Toolik Lake.

Differences in sedimentation rates on the east and west side of the lake's main basin reflect different depositional regimes (Figure 4-3). The east side has higher sedimentation rates due to its proximity to the major inlet streams and an under ice pattern of flow which carries spring runoff preferentially on that side of the lake (Hobbie et al., 1983).

In any study of sedimentation rates, it is valuable to have a second method of sediment dating to verify the rates. Carbon-14 dating was used by Dr. P. Colinvaux (unpublished data) to obtain the age of the first sediment deposits in Toolik Lake after the retreat of glaciers. Approximately 1.0 to 2.0 m of sediment have accumulated in the major basins over time, and sedimentation rates range from 0.010 to 0.017 cm yr<sup>-1</sup>, averaging  $0.013 \pm 0.002$  cm yr<sup>-1</sup> (n=6). The rate of sedimentation deep in the T80 cores ranges from 0.005 to 0.024 cm yr<sup>-1</sup>, averaging  $0.016 \pm 0.008$  cm yr<sup>-1</sup>, a value very similar to that from C-14. This agreement supports the validity of the Pb-210 sedimentation rates, and also suggests that historical sedimentation rates, on the average, are similar to those presently found in the lake.

### SUMMARY

From the data and discussion in the previous sections, it may be concluded:

1. Toolik Lake accumulates sediment at a rate comparable to Char Lake, but considerably lower than most other lakes.
2. The input of Pb-210 to Toolik Lake is very low.
3. Higher rates of sedimentation occur on the lake's east side, a result of the proximity to major inlets and the water flow patterns under spring ice.
4. Because of the remobilization of Ra-226, supported Pb-210 concentrations are not constant, but sedimentation rate determinations are not severely affected.
5. Aluminum or some other "conservative" parameter can be used to correct for sediment mass changes that result from the diagenetic redistribution of Mn and Fe.

## CHAPTER 5    CHEMICAL REACTION BETWEEN PORE FLUIDS AND LAKE SEDIMENT

### LIST OF TERMS USED IN CHAPTER 5

$a_{AB}$	= activity of complex AB
$C$	= concentration of interstitial solute ( $\mu\text{mol cm}^{-3}$ )
$C_{Al}$	= solid phase Al concentration ( $\text{mg cm}^{-3}$ )
$C_{Mn:Al}$	= solid phase Mn:Al ratio ( $\mu\text{mol Mn (mg Al)}^{-1}$ )
$C_s$	= concentration of "excess" or diagenetically mobile solid phase component ( $\mu\text{mol cm}^{-3}$ )
$D_4$	= tracer diffusion coefficient at 4°C ( $\text{cm}^2 \text{yr}^{-1}$ )
$D_s$	= effective diffusion coefficient corrected for tortuosity ( $\text{cm}^2 \text{yr}^{-1}$ )
$f$	= individual ion activity coefficient
$I$	= ionic strength (M)
$IAP$	= ion activity product
$K_2$	= second dissociation constant for $\text{H}_3\text{PO}_4$
$K_3$	= third dissociation constant for $\text{H}_3\text{PO}_4$
$K_{ox}$	= first order metal oxidation rate constant ( $\text{yr}^{-1}$ )
$K_{red}$	= first order metal reduction rate constant ( $\text{yr}^{-1}$ )
$K_{sp}$	= solubility product
$m_i$	= molarity of species i
$pIAP$	= negative log of the ion activity product
$R_d$	= rate of dissolution ( $\mu\text{mol cm}^{-3} \text{yr}^{-1}$ )
$R_{pc}$	= rate of phase change ( $\mu\text{mol cm}^{-3} \text{yr}^{-1}$ )

$T_d$	= residence time of solid phase diagenetic oxides (yr)
$t$	= time (yr)
$w_{Al}$	= mass sedimentation rate of Al ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ )
$w_d(x)$	= rate of burial of sediment below horizon $x$ ( $\text{cm yr}^{-1}$ )
$x$	= depth below the sediment-water interface (cm)
$z$	= charge of species $i$
$\phi$	= porosity ( $\text{cm}^3 \text{ H}_2\text{O}$ ) / ( $\text{cm}^3$ wet sediment)

## INTRODUCTION

The investigation of pore water chemistry in aquatic sediments can provide valuable insight into early diagenetic processes (Jones and Bowser, 1978). Relatively small changes in solid phase chemical composition cause large changes in pore water solute concentrations. Changes in the composition of pore fluids result in chemical gradients which can be of use in understanding solid-solution interaction (Froelich et al., 1979). The investigation of pore water P, Mn and Fe distributions in Toolik Lake sediment provides a quantitative aspect to the study of diagenetic processes. Three important questions to be addressed in this chapter are:

1. Are authigenic Fe(II) or Mn(II) mineral phases forming in Toolik Lake sediments?
2. Is a reduction/diffusion/oxidation model of Mn and Fe crust formation applicable to these sediments? Can this model account for the formation of P enriched zones?
3. What processes regulate pore water Mn, Fe and P concentrations?

Comparison of the concentrations of solutes with those expected from literature solubility products (question 1) can help determine whether authigenic mineral formation is possible. Application of this technique to a wide variety of sedimentary environments has proven its utility for the study of authigenic mineral formation and the regulation of pore water solute concentrations (Nriagu and Dell, 1974; Tesenow, 1974; G.R. Holdren, 1977; Emerson and Widmer, 1978).

The second question will be addressed by numerical modelling of

changes in pore water and solid phase chemical distributions. These models can include terms for diffusion, advection, sediment mixing, radioactive decay and reaction between solids and solution (Berner, 1980). A steady state numerical model has been developed for Toolik Lake sediments, and a reaction-diffusion mechanism of crust formation is demonstrated. This model also provides information on the locations within the sediment column of important diagenetic processes. The final question (pore water solute regulation) uses the results of the solubility calculations and numerical modelling to provide insight into the mechanisms which control pore water solute concentrations.

The use of pore water profiles to examine sequences of diagenetic reactions has been developed most completely by Froelich et al., (1979). A schematic was developed, based on the reactions presented in Table 3-3, which shows the expected pore water trends in dissolved  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$  and  $Fe^{2+}$  as successive electron donors are utilized during organic matter oxidation. A similar schematic can be drawn which shows predicted pore water trends in Toolik Lake profundal sediments (Figure 5-1). The reactions that are shaping these profiles are indicated. Elevated concentrations of pore water  $Mn^{2+}$ ,  $Fe^{2+}$  and  $PO_4$  are expected below solid phase maxima. Upward diffusion of solutes maintains solid phase enrichments in the same horizon (relative to the interface). For inorganic P, two modes of association with the sediment are investigated: adsorption to Fe(III) oxyhydroxides and formation of Fe(II), Mn(II) or Ca phosphate minerals. The reactions presented in Figure 5-1 represent a small subset of the possible

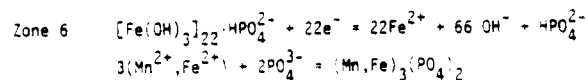
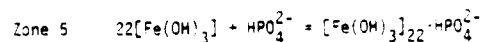
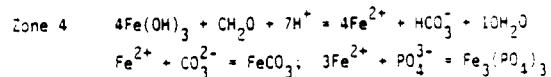
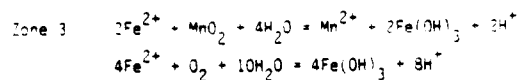
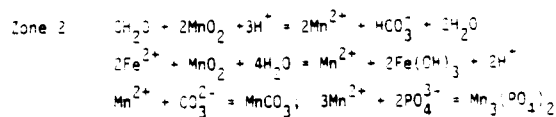
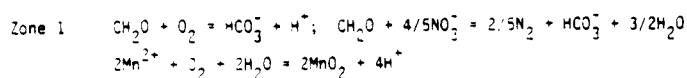
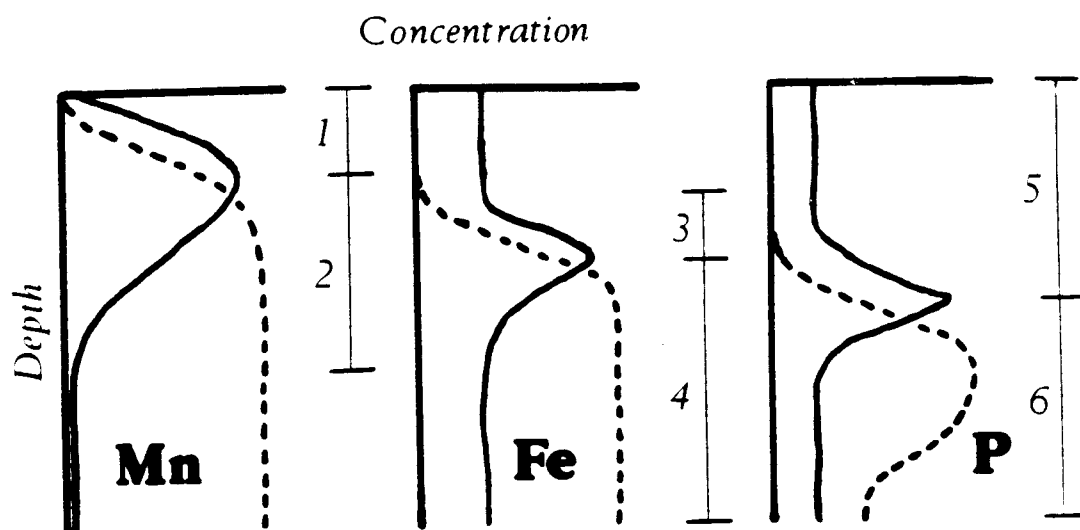


Figure 5-1. Sediment reaction sequences for Toolik Lake profundal sediments. A series of sediment zones are shown and the characteristic reactions in each zone are presented.



diagenetic reactions occurring in Toolik Lake sediment. Each reaction which affects pore water and solid phase Fe, Mn and P distribution will be examined.

A single transect of cores collected in May and June 1980 provides the information about pore water concentrations and trends. Low rates of sedimentation and relatively small seasonal changes in hypolimnetic temperatures and dissolved oxygen allow the use of pore water profiles from the spring to be used to approximate the year round profiles. Littoral zone cores are more variable in interstitial water chemistry throughout the season than profundal zone cores (Klingensmith, 1981). Lateral heterogeneity in nearshore areas is high, making determination of littoral zone temporal variation difficult.

#### METHODS

A K-B corer modified to accept 6.6 cm inner diameter core liners was used to obtain all the cores used for interstitial water study. These were collected in May and June 1980 through holes drilled in the lake ice. The corer was slowly lowered, not dropped, into the soft sediment, and cores 25 to 45 cm long were obtained. Several cores were collected from each site, all within 2.0 m of each other. The first core was used for the determination of dissolved and solid phase Mn, Fe, P and major cations, as well as pH and Eh. The second core was used for the determination of ammonia, Si, dissolved inorganic C (DIC) and usually pH. The third core from each site was used for the

determination of Pb-210 (Chapter 4), solid phase P, Mn, Fe, Al, Ca, Mg, K, total carbonate, organic C, N and trace elements (Chapter 6). Processing of cores for interstitial water analysis of Mn Fe and P commenced within 0.5 h of collection. Rapid handling kept the core cool throughout the squeezing process. The loading of squeezers and the determination of pH and pE were done within an N<sub>2</sub> filled glovebag which had been inflated and purged 3 times to purge oxygen. An Orion (96-78) combination calomel/platinum redox electrode and a combination pH electrode were directly inserted into the sediments and readings were taken when drift was minimal. Performance of the redox electrode was periodically checked with standard solutions following the manufacturer's instructions, and pH buffers of 4 and 7 were used to standardize the pH electrode for each core. Readings taken in and out of glove bags gave similar results; air oxidation was not a problem in the measurement of Eh or pH.

Reeburgh (1967) plastic core squeezers with Gelman A/E glass fiber filters were used throughout this study. The squeezers and the filters were purged with N<sub>2</sub> gas prior to the addition of mud. Within the glovebag, a plastic spatula was used to transfer sediment from the core liner to the squeezers. The top four sections of each core were squeezed in 1.0 cm thick sections, with thicker sections squeezed deeper in the core.

The squeezing was done outside the glove bags because of difficulty in arranging the squeezers inside the bag. At no time was the sediment exposed to air, and squeezing was very rapid because of

high porosities. Small volumes of interstitial water were pipetted immediately into colorimetric reagents for the analysis of phosphate (Strickland and Parsons, 1968) and ferrous Fe (Gibb, 1979).

Samples for the analysis of Mn and major cations were put in 15 ml polyethylene bottles and acidified with 10 to 20 ul of concentrated  $\text{HNO}_3$ . A Perkin-Elmer 603 atomic absorption spectrophotometer was used for metals analysis, with lanthanum added to samples to suppress interferences in the analysis of Ca and Mg.

Glove bags were not used to extrude the second interstitial water core from each site. Dissolved inorganic C (DIC) was estimated using the headspace technique of Hesslein (1976) in which 4.0 ml of pore water is injected into evacuated serum vials containing 10 ul concentrated  $\text{H}_2\text{SO}_4$ . The headspace was sampled with a syringe and injected into a thermal conductivity gas chromatograph (Carle GC 8700) with Poropak Q columns for  $\text{CO}_2$  analysis. Pure  $\text{CO}_2$  was injected into vials for calibration. Problems with calibration and reproducibility of the method suggest the results are good to  $\pm 20\%$ .

Samples for  $\text{NH}_4^+$  and Si (silicic acid) analysis were frozen, transported to Fairbanks, and analyzed on a Technicon AutoAnalyzer using the phenolphthorite  $\text{NH}_4^+$  method of Slawyk and MacIsaac (1972) and the Si method of Armstrong et al. (1967). Ammonium was analyzed immediately after defrosting the samples, and Si was determined on samples stored at room temperature for several days prior to analysis to minimize polymerization problems.

In 1981, four additional cores (collected with G.W. Kipphut) were

squeezed for DIC,  $\text{NH}_4^+$  and Si. All methods remained the same except that the DIC measurement was by Stainton's (1973) syringe gas stripping method. The precision of the DIC determinations was much improved (coefficient of variation < 10%).

#### PORE WATER RESULTS

Concentrations of pore water Mn range from less than 1.0  $\mu\text{M}$  to 360  $\mu\text{M}$  (Figure 5-2). In the two cores from the littoral zone (T80-3.5A, T80-5.5A), concentrations of interstitial Mn near the interface are somewhat higher than values for profundal surficial sediments (except T80-11.0A), although concentrations deep in profundal cores are much higher. The profundal sediments have steep pore water Mn gradients in the top 5.0 cm of the cores and the littoral sediments have small pore water gradients as well as much lower solid phase Mn concentrations. All the profundal sediments have Mn and Fe crusts. The two cores from 18.0 m have similar interstitial water Mn trends, although T80-18.0C has slightly lower values deep in the cores.

Pore water  $\text{Fe}^{2+}$  concentrations range from 0 to 470  $\mu\text{M}$  (Figure 5-3), generally increasing with distance below the sediment-water interface. The Fe pore water profiles are not as smooth as those for Mn, and the largest increases usually occur several centimeters below the large pore water Mn increase, especially in profundal sediments. These increases most often occur in conjunction with the bottom of the Fe crust.

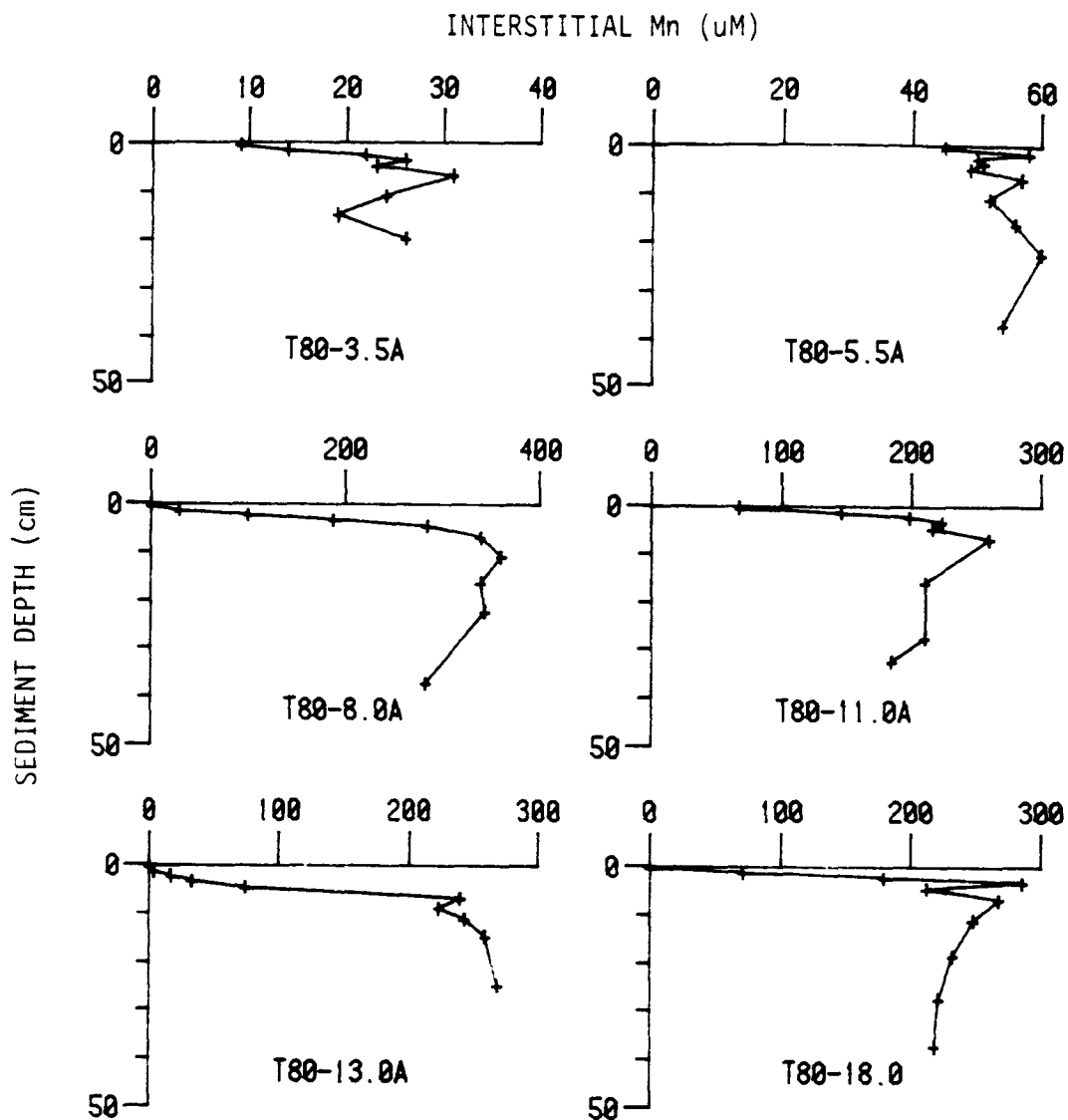


Figure 5-2. Pore water manganese data, 1980 transect. All concentrations in uM.

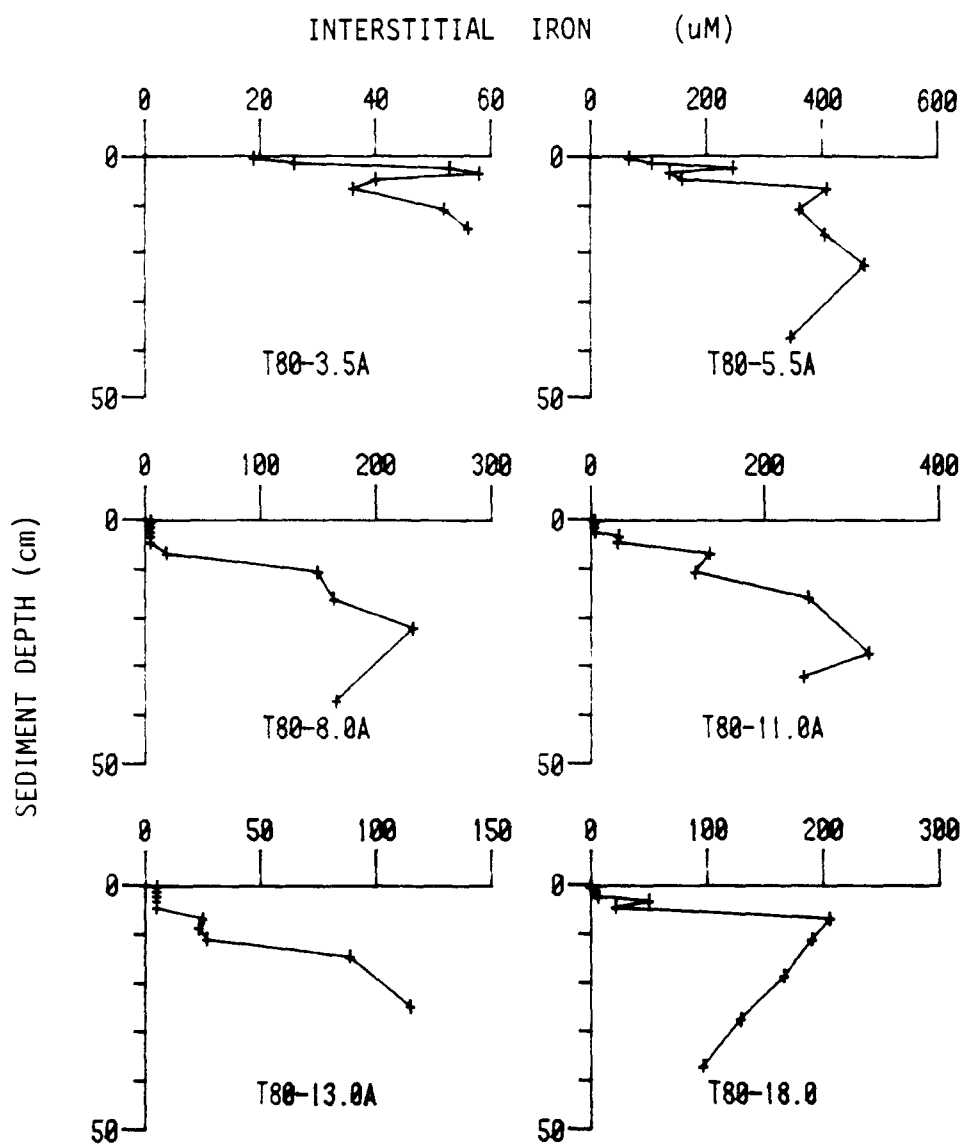


Figure 5-3. Pore water iron data, 1980 transect. All concentrations in uM.

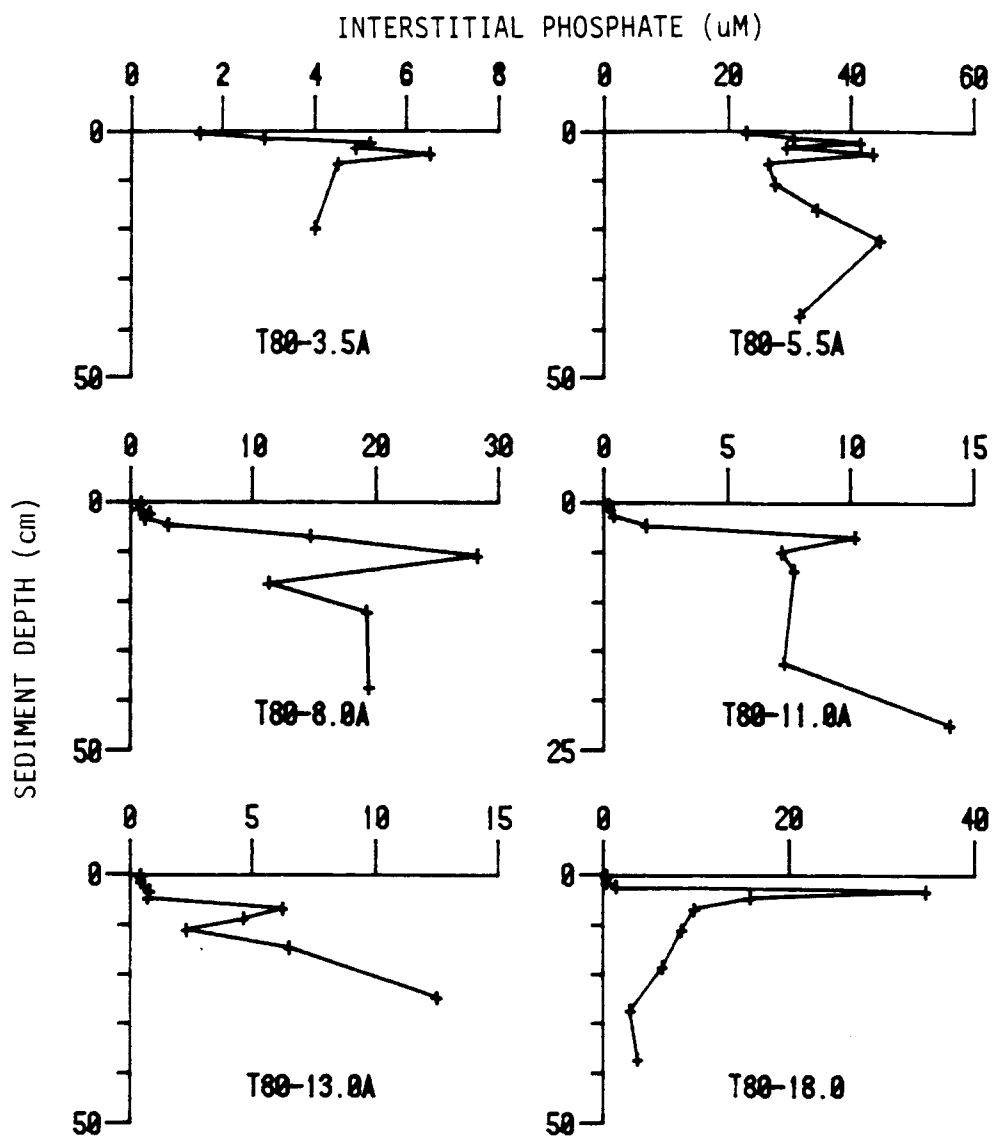


Figure 5-4. Pore water phosphorus data, 1980 transect. All concentrations in uM.

Pore water phosphate ( $\text{PO}_4$ ) concentrations range from  $< 1 \text{ uM}$  up to  $45 \text{ uM}$  (Figure 5-4), concentrations much higher than found in the water column. Cores T80-3.5A and T80-5.5A have very high concentrations of  $\text{PO}_4$  at the sediment-water interface. Increased  $\text{PO}_4$  concentrations are found in all profiles where Fe concentrations increase, especially in T80-18.0C.

Oxidation of reduced species during pore water squeezing can create problems in obtaining reliable data (Bray, 1973). The lack of smoothness in the interstitial water profiles is most likely a result of the influence of Fe(II) oxidation. Interstitial water analyses without glovebags in 1979 (J. Cornwell, unpublished data) gave Mn and  $\text{PO}_4$  profiles similar to those in 1980. The Fe values were much higher (up to  $2200 \text{ uM}$  based on atomic absorption for analysis). The absence of smooth pore water Fe data most often occurs in the vicinity of the solid phase Fe crust and probably results from the presence of Fe(III)-Fe(II) colloidal complexes. Experiments in 1979 show that filter pore size does not appreciably alter the amount of colloidal orange material in pore water (J. Cornwell and R.J. Barsdate, unpublished observation). This orange colloid may have significant amounts of inorganic P adsorbed onto it. This pool of inorganic P is solubilized and analyzed as  $\text{PO}_4$ . The  $\text{PO}_4$  data is least reliable for the sections in and immediately below the Fe crust, especially sections having significant orange color. The adsorptive properties of these colloids may also exert some effect upon the analytical Mn concentrations.



The profiles of pH for the interstitial water cores are similar to those described earlier (Chapter 3). Littoral zone sediment pH's increased from 6.6 at the interface to 6.9 at depth and profundal pH's increased from 6.6 at the interface to approximately 7.6 at depth. The values of pE decreased below the sediment water interface for all of these cores, with large decreases occurring immediately below Mn and Fe crusts. The two littoral cores had lower interface pE values than did the profundal cores.

The distribution of some other pore water constituents will be described briefly here. Major cations were somewhat enriched in interstitial water relative to the water column, with Mg enriched 0 to 20%, Ca enriched 30 to 40% and K enriched 250%. Results for Na were extremely variable and are not reported. No large changes in the concentrations of the major cations occur within any core. Average surficial  $\text{NH}_4^+$  concentrations are  $5 \pm 3$  uM with maximum concentrations of 50 uM found deep in some cores. Pore water  $\text{NO}_3^-$  concentrations measured by Klingensmith (1981) were always low, with surficial sediments having less than 5 uM and deeper sediments having undetectable concentrations. Interstitial Si increases with depth in most cores, with the highest concentrations occurring in littoral sediments, presumably because of dissolution of benthic diatoms.

Concentrations of DIC ranged from 700 to 1500 uM near the interface to values up to 3000 uM at depth. Concentrations of 600 to 700 uM DIC were found in the water column at the time of sampling (S. Whalen, personal communication). Two cores from the 18.0 m station,

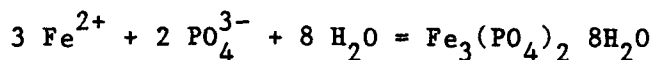
one taken by me in 1980 and another with G. W. Kipphut in 1981, have very similar DIC profiles.

## AUTHIGENIC MINERAL FORMATION

### Use of the Thermodynamic Approach: Applications and Limitations

Equilibrium calculations are used in this study to examine the formation of authigenic Mn(II), Fe(II) and P minerals and the mechanisms which regulate pore water  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{PO}_4$  concentrations. Other studies (especially Nriagu and Dell, 1974; Emerson, 1976; Emerson and Widmer, 1978; Tessenow, 1974; G.C. Holdren, 1977) have used solubility calculations to predict formation of authigenic minerals in lacustrine sediments, and similar studies in estuarine and oceanic sediments have provided information on the formation of authigenic Mn, Fe and P minerals (G.R. Holdren, 1977; Bray, 1973; Aller, 1980a; 1980b; Murray et al., 1978).

The saturation state of pore water may be estimated by comparing the ion activity product (IAP) of pore water to the  $K_{sp}$  for a given phase. An ion activity product is calculated by using the analytically determined concentrations of pore water solutes to calculate the activity of each species in solution. The activity of each solute is then compared to the concentrations expected from literature solubility data. Saturation may be determined in the following manner for vivianite:



$$(1) \text{ IAP} = (a_{\text{Fe}^{2+}})^3 * (a_{\text{PO}_4^{3-}})^2$$

$$\text{IAP} > K_{sp} \quad \text{oversaturation}$$

$$\text{IAP} = K_{sp} \quad \text{saturation}$$

$IAP < K_{sp}$  undersaturation

The saturation state provides information on the possibility of formation of authigenic phases. Evidence of this kind is not sufficient to prove the occurrence of authigenic minerals (Emerson, 1976). Indeed, hydroxyapatite and siderite commonly are oversaturated in lake sediment pore water, but no direct evidence exists for the precipitation of these mineral forms in modern lacustrine sediments (Syers et al., 1973; Jones and Bowser, 1978; Kelts and Hsu, 1978).

#### Calculation of Ion Activity Products

The thermodynamic constants used in this study are presented in Table 5-1. Most of the constants presented here correspond to those used by Emerson (1976) and wherever possible, constants valid at 5°C are used.

The calculation of IAP's involves the estimation of the ionic strength so that activity corrections may be made. Chloride and sulfate were not measured in this study so their concentrations must be estimated from the charge imbalance in several cores. From this calculation, the charge associated with the unmeasured anions is estimated to be approximately  $0.4 \pm 0.2$  mM, which could yield 0.4 mM chloride or 0.2 mM sulfate.

Ionic strength may be computed from:

$$(2) \quad I = \sum 0.5 * m_i * z_i^2$$

Table 5-1. Equilibrium constants at infinite dilution used in this study.

No.	Equation	Temp. (°C)	pKsp	References
1.	$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3(\text{s})$	5	10.5	Cook, 1981
2.	$\text{Mn}^{2+} + \text{CO}_3^{2-} = \text{MnCO}_3(\text{s})$	10	10.5	Robbins and Callender, 1975
3.	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3(\text{s})$	5	8.4	Jacobson and Langmuir, 1974
4.	$5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- = \text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s})$	5	56.	Kramer, 1964
5.	$\text{Fe}^{2+} + 2\text{Ca}^{2+} + 2\text{PO}_4^{3-} = \text{FeCa}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$	25	34.0	Nriagu and Dell, 1974
6.	$3\text{Mn}^{2+} + 2\text{PO}_4^{3-} + 3\text{H}_2\text{O} = \text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{s})$	5	31.8	Tessenow, 1974
7.	$3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O} = \text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$	5	33.5	Tessenow, 1974
8.	$\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$	5	6.517	Stumm and Morgan, 1981
9.	$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	5	10.557	Stumm and Morgan, 1981
10.	$\text{H}_2\text{PO}_4^- = \text{HPO}_4^{2-} + \text{H}^+$	5	7.28	Tessenow, 1974
11.	$\text{HPO}_4^{2-} = \text{PO}_4^{3-} + \text{H}^+$	5	12.65	Tessenow, 1974
12.	$\text{Fe}^{2+} + \text{HPO}_4^{2-} = \text{FeHPO}_4$	25	-3.6	Nriagu, 1972
13.	$\text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4$	25	-2.70	Emerson, 1976
14.	$\text{Mg}^{2+} + \text{HPO}_4^{2-} = \text{MgHPO}_4$	25	-2.91	Emerson, 1976
15.	$\text{Fe}^{2+} + \text{H}_2\text{PO}_4^- = \text{FeHPO}_4^+$	25	-2.7	Nriagu, 1972
16.	$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaHPO}_4^+$	25	-1.4	Emerson, 1976
17.	$\text{Mn}^{2+} + \text{HCO}_3^- = \text{MnHCO}_3^+$	25	-1.95	Morgan, 1967

where  $m_i$  is the molarity of species  $i$  and  $z_i$  is its charge. The contribution of unmeasured anions is approximately  $0.3 \pm 0.1$  mM. The uncertainty of the ionic strength calculation is less than 10 or 20% of the ionic strength, which ranges from 1.2 to 3.5 mM. The individual ion activity coefficients for charged species are estimated from the Guntelberg approximation (Stumm and Morgan, 1981):

$$(3) \log f = -0.5 * z^2 * \sqrt{I} / (1 + \sqrt{I})$$

where  $z$  is the charge of the solute species,  $I$  is the ionic strength and  $f$  is the individual ion activity coefficient. Cation activities were estimated directly from analytical concentrations and the activity coefficients, neglecting complexation reactions for all but  $Mn^{2+}$ . Davison (1979) has shown that at an ionic strength of 2.0 mM and pH of 8, over 96% of  $Fe^{2+}$  is uncomplexed, eliminating the need for consideration of side reactions for Fe. Manganese(II)-bicarbonate complexes (table 5-1, equation 17) can account for up to 15% of aqueous Mn(II) (but only 3% of bicarbonate). Calcium-bicarbonate complexes account for less than 1% of total interstitial Ca.

The activity of  $CO_3^{2-}$  in pore water was estimated from DIC, activity coefficients and  $H_2CO_3$  dissociation constants. The activity of  $PO_4^{3-}$  was estimated by two techniques. The first includes ionic strength corrections but not reactions which complex phosphate in solution:

$$\text{Total } PO_4 = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$(4) \quad a_{\text{PO}_4^{3-}} = [\text{total PO}_4 / (1/f_{\text{HPO}_4^{2-}} + a_{\text{H}^+}/(K_2 * f_{\text{H}_2\text{PO}_4^-}))] * K_3/a_{\text{H}^+}$$

where total P is the analytical  $\text{PO}_4$  concentration,  $f_{\text{HPO}_4^{2-}}$  and  $f_{\text{H}_2\text{PO}_4^-}$  are activity coefficients, and  $K_2$  and  $K_3$  are the second and third dissociation constants for  $\text{H}_3\text{PO}_4$ . This is similar to the calculations of Nriagu and Dell (1974).

The second method of IAP calculation includes complex formation and ionic strength corrections and uses the following mass balance:

$$\begin{aligned} \text{Total PO}_4 = & [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{PO}_4^{3-}] + [\text{CaHPO}_4] + [\text{CaH}_2\text{PO}_4^+] + \\ & [\text{MgHPO}_4] + [\text{FeH}_2\text{PO}_4^+] + [\text{FeHPO}_4] \end{aligned}$$

This is the approach taken by Emerson (1976), and it depends upon the calculation of "apparent" equilibrium constants (Stumm and Morgan, 1981) corrected for ionic strength. Side reaction coefficients (Elder, 1975) were used to determine the fraction of uncomplexed  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  (using equations 10-16 in Table 5-1). From mass balance considerations and the dissociation constants of  $\text{H}_3\text{PO}_4$ , the activity of  $\text{PO}_4^{3-}$  may be estimated. Formation of metal-organic complexes in pore water has not been considered in this study, but as in the study of Emerson (1976), it is unlikely that they constitute a very large proportion of total metals.

Ion activity products were calculated for siderite ( $\text{FeCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ), calcite ( $\text{CaCO}_3$ ), vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), reddingite ( $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ ), anapaite ( $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) and hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) and are presented as the negative log of IAP

(pIAP). Some pH measurements and all of the DIC and  $\text{NH}_4^+$  data are from cores taken in parallel with the metals- $\text{PO}_4$  core. Lateral heterogeneity in the chemistry of these sediments may have a small effect upon the results presented here.

The activity of  $\text{PO}_4^{3-}$  calculated with and without consideration of soluble complexes yields different pIAP's for the metal phosphates in core T80-18.0B (Table 5-2). The  $\text{PO}_4^{3-}$  activity is 4 to 125% higher in the uncomplexed case, yielding pIAP differences of 0.0 to 0.7 for anapaite, reddingite and vivianite, and 0.1 to 1.0 for hydroxyapatite. The concentration of  $\text{FeHPO}_4$  is up to 1.3 times the concentration of uncomplexed  $\text{HPO}_4^{2-}$ , with the concentration of  $\text{CaHPO}_4$  averaging 0.3 times the  $\text{HPO}_4^{2-}$  concentration.

The first method of calculating the  $\text{PO}_4^{3-}$  activity is used to calculate the IAP's for several reasons:

1. Few of the constants for  $\text{PO}_4$ -metal complexes are available for low temperatures.
2. The two methods agree reasonably well, especially when the large variations in the literature values of metal phosphate  $K_{sp}$ 's are considered.
3. Tessenow's (1974)  $K_{sp}$  determinations do not suggest a need for consideration of soluble Fe or Ca complexes.

Changes in pH can exert a significant influence on the calculation of IAP's. The effect of a 0.1 pH change on pIAP is approximately 0.1 for carbonates, 0.5 for apatite and 0.25 for the other phosphates, including vivianite. A change in ionic strength of 1.0 mM results in



Table 5-2. Ion activity product data for core T80-18.0C. Two methods of calculating  $\text{PO}_4^{3-}$  were used in this study, the first method (A) uses only ionic strength for calculation purposes, and the second method (B) uses both ionic strength and complex formation calculations. The phases considered are siderite (SIDER), rhodochrosite (RHODO), hydroxyapatite (APATI), vivianite (VIVI), reddingite (REDD), calcite (CALC) and anapaite (ANAPA).

Depth (cm)	mM Ionic Strength	SIDER	RHODO	A APATI	B APATI	A VIVI	B VIVI	A REDD	B REDD	CALC	A ANAPA	B ANAPA
0.5	1.2	13.8	13.8	67.3	67.4	45.7	45.7	45.7	45.7	11.3	40.7	40.6
1.5	1.4	12.9	11.7	66.6	66.7	43.4	43.4	39.7	39.8	11.0	39.7	39.6
2.5	1.8	11.9	10.5	61.7	61.9	39.7	39.8	35.6	35.7	10.3	36.5	36.4
3.5	2.2	10.8	10.0	56.3	56.7	33.7	34.0	31.6	31.8	10.0	32.4	32.1
5.0	2.0	10.7	9.7	55.6	55.9	34.4	34.6	31.6	31.9	9.6	32.4	32.2
7.0	2.6	9.5	9.5	55.7	56.7	31.6	32.3	31.4	32.2	9.4	32.1	31.4
11.3	2.5	9.6	9.5	55.7	56.7	31.8	32.5	31.6	32.3	9.4	32.1	31.4
18.8	2.4	9.6	9.6	56.4	57.3	32.3	33.0	32.1	32.7	9.4	32.5	31.9
27.5	2.2	9.8	9.6	57.6	58.4	33.3	33.9	32.8	33.3	9.5	33.3	32.8
37.5	2.2	9.9	9.6	57.1	57.8	33.5	34.0	32.6	33.1	9.4	33.1	32.6

pIAP changes of 0.02 for the carbonates, 0.15 for apatite and 0.1 for the other phosphates.

#### Ion Activity Product Results

Values of pIAP generally decrease (IAP increases) with increasing sediment depth as solutes become more concentrated. Apatite, vivianite, reddingite and anapaite are all close to saturation (Table 5-2). When all the assumptions associated with IAP calculation are taken into account, having apatite within 1.0 pIAP of its  $K_{sp}$ , the tertiary metal phosphates within 0.5 pIAP and the carbonates within 0.25 pIAP means that the interstitial water is not distinguishably different from saturation. Of the mineral phases considered here, only calcite, which is undersaturated, and rhodochrosite and siderite, which are supersaturated, are not near equilibrium. Vivianite is undersaturated at the interface, slightly supersaturated between 7 and 11 cm, and near equilibrium at greater depths.

Table 5-3 summarizes the pIAP value data for each core, with each pIAP value coming from near the bottom of the core. Siderite appears to be at saturation throughout CB80-8.0, a core from the east side of the lake. In T80-3.5, siderite is undersaturated and in all others it is supersaturated. Siderite usually does not form in modern lacustrine sediments (Kelts and Hsu, 1978) and supersaturation does not necessarily indicate that the phase is forming. Rhodochrosite is supersaturated in profundal sediments, perhaps because of slow crystal formation kinetics.

Table 5-3. The pIAP values for the deepest sections of cores.

Core ID	$\text{FeCO}_3$	$\text{MnCO}_3$	$\text{Fe}_3(\text{PO}_4)_2$	$\text{Mn}_3(\text{PO}_4)_2$	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$
T80- 3.5A	11.0	11.4	36.8	37.7	61.5
T80- 5.5A	10.0	10.9	32.2	34.9	58.2
T80- 8.0A	9.4	9.3	31.7	31.2	55.1
T80- 11.0A	9.5	9.8	31.8	32.7	57.0
T80- 13.0A	9.6	9.3	32.1	31.6	55.8
T80- 18.0A	9.5	9.7	31.4	31.6	55.2
T80- 18.0C	9.8	9.6	33.4	32.7	57.5
CB80- 8.0A	10.5	11.7	32.5	36.5	58.0
$\text{pK}_{\text{sp}}$	10.5	10.5	33.5	31.8	56.0

Apatite is near saturation in all cores except for T80-3.5 and perhaps T80-5.5 and CB80-8.0. Many of the other apatite pIAP values are very close to the  $K_{sp}$ .

The  $K_{sp}$  data of Tessenow (1974) for mixed Mn-Fe phosphates at 5°C are valuable for the interpretation of vivianite and reddingite pIAP data. At a dissolved Fe:Mn ratio of 1.0, the  $pK_{sp}$  for vivianite is 32.5, one full unit below that for pure vivianite. All of these cores are near saturation with respect to vivianite (except T80-3.5), especially when the  $K_{sp}$  changes associated with increasing  $Mn^{2+}$  concentrations (Tessenow, 1974) are considered. The reddingite data in Table 5-3 indicate that all cores except T80-3.5, T80-5.5 and CB80-8.0 are close to saturation. The reddingite  $K_{sp}$  also varies with the Fe:Mn ratio (Figure 5-5). Only T80-3.5 is not near equilibrium with respect to the  $Fe^{2+}-Mn^{2+}-PO_4^{3-}-(Fe,Mn)_3(PO_4)_2$  system.

#### Authigenic Phases in Toolik Lake

The saturation state can provide information on the possibility of authigenic mineral formation, but other evidence such as X-ray crystallography, chemical analysis or microprobe analysis must confirm the existence of the authigenic phase. In this study, chemical data on the solid phase is used in conjunction with energy dispersive X-ray analysis (EDXRA).

The relevant solid phase data for the Toolik Lake 18.0 m station are presented in Figure 5-6. Concentrations of carbonate in Toolik sediment are highest ( $0.3 \text{ mmol g}^{-1}$ ) in the Mn and Fe crusts, and lower

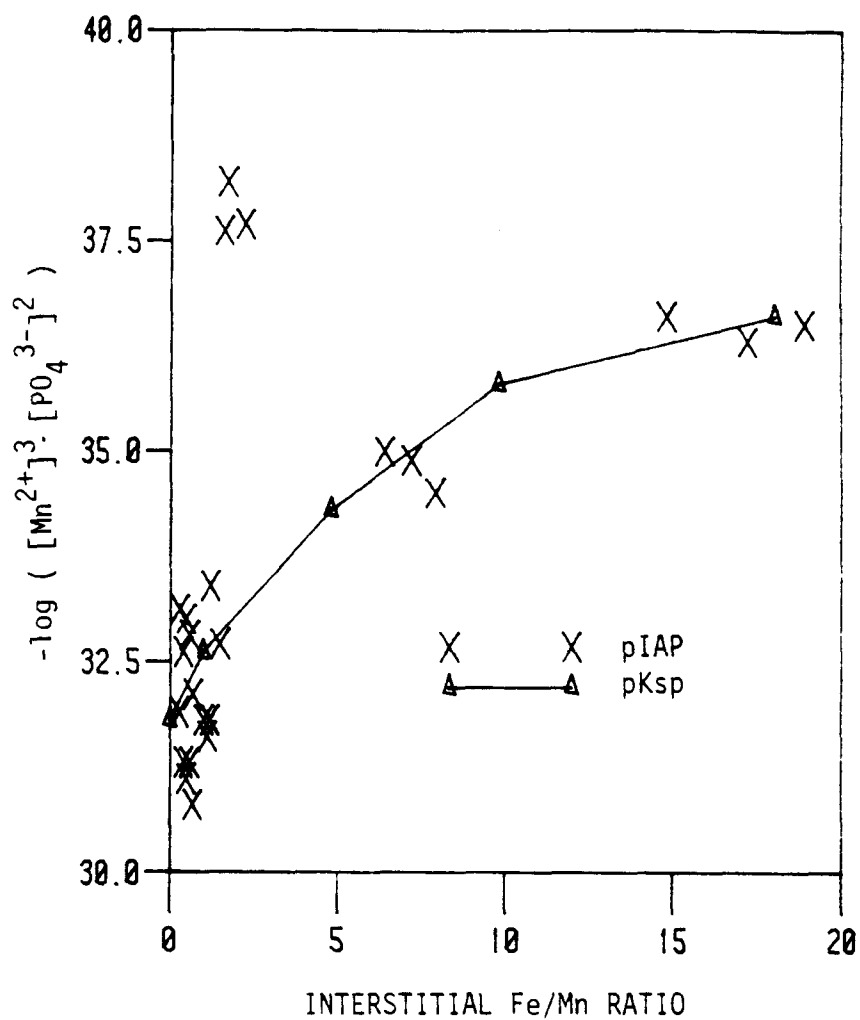


Figure 5-5. Reddingite pKsp plotted against the ratio of  $\text{Fe}^{2+}$  to  $\text{Mn}^{2+}$  (Tessenow, 1974). The X's are pIAP values for the bottom three sections of all cores analyzed for interstitial water chemistry.

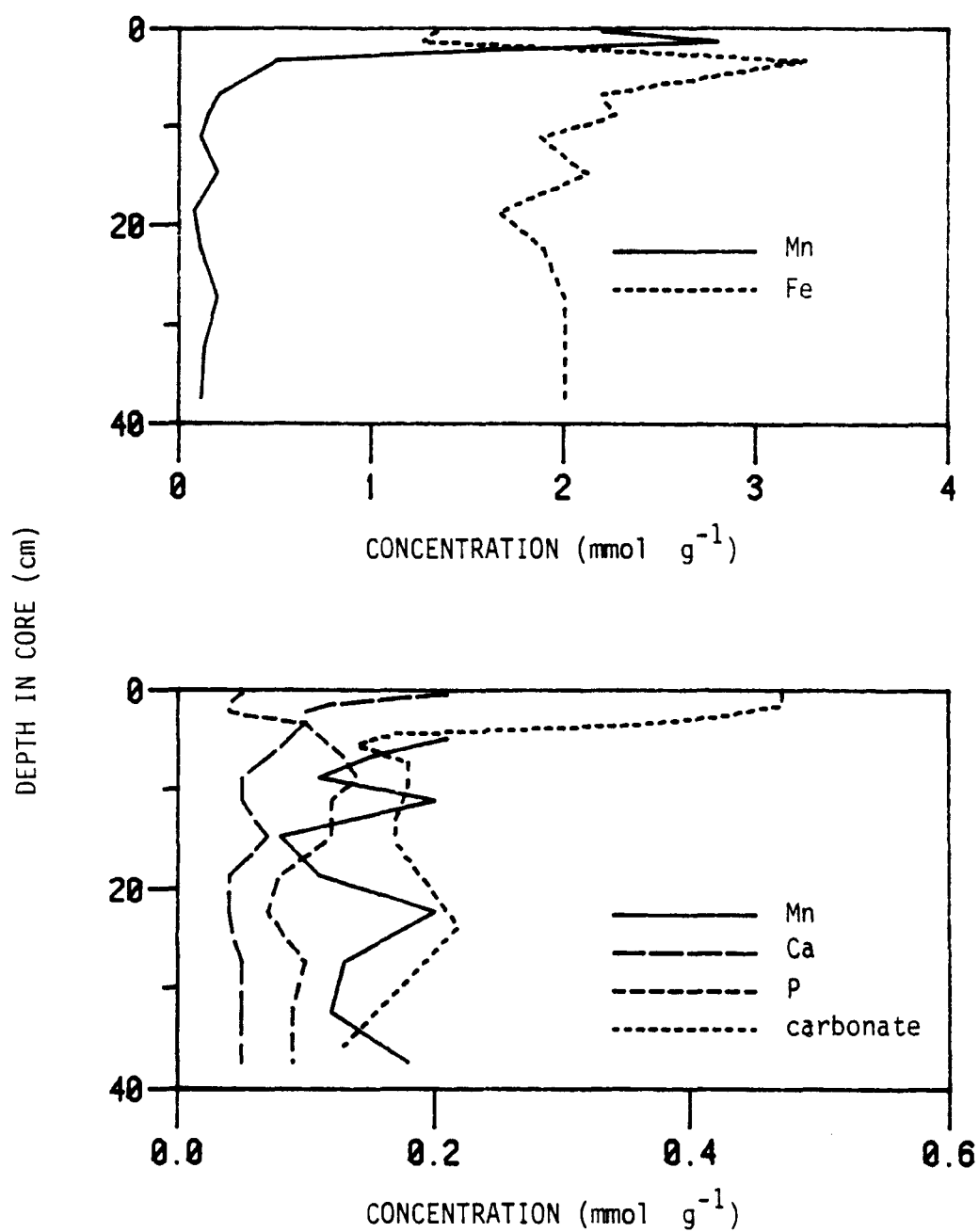


Figure 5-6. Solid phase P, Mn, Fe and carbonate plotted versus depth for the 18.0 m. location.

beneath the crusts. This is an enigma since the crusts are undersaturated with respect to Mn and Fe carbonates and the region below the crust is supersaturated! Deeper in the core, the concentration of sediment carbonate is similar to that of Mn and 10 to 15 times lower than the Fe concentration. Carbonates below the metal oxide crusts could account for all of the solid phase Mn or a small fraction of the Fe. Carbonate concentrations are severalfold higher than Ca concentration, and pure calcium carbonates cannot be the primary carbonate phase in these sediments. Mixed Mn(II)-Fe(II)-Ca carbonate phases may well be forming in these sediments, but they constitute only a small part of the sediment.

Phosphate minerals regulate pore water  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{PO}_4$  concentrations in some sediment environments. The solid phase data for Ca and P provide few clues with regard to hydroxyapatite formation and only the IAP value suggests that this mineral is forming. This is not the case for mixed Mn-Fe phosphates. White vivianite nodules less than 0.5 cm in diameter were found. These nodules were very porous and turned blue upon air oxidation of Fe(II), a characteristic of vivianite (McCammon and Burns, 1980). Elemental analysis of individual nodules (via EDXRA) showed that P and Fe were the major components of this blue material, with Mn being present in smaller quantities. Low concentrations of Ca rule out a significant role for mixed Fe(II)-Mn(II)-Ca phosphates and anapaite in these concretions.

Analyses of the bulk sediment does not provide any indication that Fe-Mn phosphates are forming in Toolik Lake sediment. Manganese

phosphates cannot account for a very high fraction of the total sediment Mn, because Fe is the dominant component of the phosphate concretions. Vivianite can constitute less than 5% of sediment Fe deep in these cores, with the remainder being of unknown composition.

#### Regulation of Pore Water Chemistry

Only the Mn-Fe-phosphate system has been shown to produce authigenic minerals in Toolik Lake. Interstitial  $\text{PO}_4$  is low (relative to  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ) suggesting that the  $\text{PO}_4$  concentrations are regulated by vivianite formation. Not enough Mn or Fe phosphate could be produced to substantially affect  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  concentrations.

Pore water  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  concentrations decrease with increasing depth in several cores (Figures 5-2,5-3) suggesting a removal mechanism not explained in the previous discussion. Carbonate phases may partially account for this decrease, but processes such as adsorption or precipitation of alternate phases not considered here may be occurring to a small extent.

Vivianite has generally been found in eutrophic freshwaters characterized by extremely reducing sediments and much higher concentrations of  $\text{PO}_4$  than found in Toolik Lake sediment (Tessenow 1974; Emerson and Widmer 1978; Nriagu and Dell 1974). The feature of Toolik Lake sediment that permits saturation with respect to vivianite is the almost complete retention of diagenetically mobile Fe in oxidized zones, forming a barrier to the loss of metals to the water column. Absence of sulfide production also allows the concentrations of Fe in



pore water to remain high. The Fe reduction/diffusion/oxidation cycle results in the solution of inorganic P associated with oxides, and leads to higher concentrations of  $\text{PO}_4$  in solution and the formation of reduced metal phosphates.

#### Authigenic Minerals: Conclusions

The major findings of this equilibrium treatment of chemical diagenesis are:

1. The formation of pure Fe(II) or Mn(II) carbonates does not strongly regulate pore water  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and DIC concentrations, although carbonate enrichments occur with metal oxide accumulations.
2. Anapaite and hydroxyapatite are probably not important authigenic minerals in Toolik Lake sediments.
3. Mixed Fe-Mn phosphates are being formed in Toolik Lake.
4. Formation of authigenic phosphate minerals controls pore water  $\text{PO}_4$  concentrations.
5. Iron(II)-Manganese(II) phosphates form in Toolik Lake despite low P inputs to the sediment. This is a result of strong retention of Mn, Fe and P by sediment and high concentrations of these elements below the surface oxidized zone.

## FORMATION OF METAL OXIDE CRUSTS: DIFFUSION-REACTION MODELLING

### Introduction to Diagenetic Models

In recent years, significant advances have been made in the understanding of sediment diagenesis by applying quantitative rate models to the cycling of nutrients, metals, non-metals and radionuclides in a variety of sedimentary environments (Berner, 1980). These models can provide information on the rate at which processes occur, and the location of these processes within the sediment column. The model developed for the examination of Toolik Lake diagenetic processes is used to confirm the viability of the dissolution/diffusion/precipitation mechanism of Mn, Fe and P diagenetic redistribution.

The model will initially be applied to Mn diagenesis. A large amount of effort has been put into the study of Mn diagenesis by other investigators (Robbins and Callender, 1975; G.R. Holdren, 1977; Calvert and Price, 1972; Aller, 1980b; Burdige and Gieskes, 1983) and the Toolik Lake sediment Mn cycle can be compared to a number of other studies. The model will then be applied to Fe and P diagenesis.

### Development of a Model

The model developed here is primarily intended to couple the profiles of Mn in both solid and dissolved phases with rates of sediment burial and molecular diffusion. The premise for the model is that the burial and reduction of Mn oxides results in diffusion and

oxidation of pore water  $\text{Mn}^{2+}$ . The pore water profiles of  $\text{Mn}^{2+}$  are predicted on the basis of the concentrations of Mn in cores and the sedimentation rates. The chief assumption is that the profiles of Mn in both solid and aqueous phases are time invariant.

In a sediment in which the rate of burial of pore water and sediment is low, a simple differential equation may be written (Berner, 1976):

$$(5) \quad D_s * \partial^2 C / \partial x^2 + R_{pc} = 0$$

where  $R_{pc}$  is the rate of phase change of Mn ( $\text{umol cm}^{-3} \text{ yr}^{-1}$ ),  $D_s$  is the diffusion coefficient including corrections for tortuosity ( $\text{cm}^2 \text{ yr}^{-1}$ ),  $C$  is the concentration of  $\text{Mn}^{2+}$  ( $\text{umol cm}^{-3}$ ), and  $x$  is the depth below the interface (cm). This model includes terms for the dissolution and precipitation of Mn oxides, but not for the formation of Mn(II) phases below the oxidized zone.

The evaluation of the phase change term may be treated in a manner analogous to that of Robbins and Callender (1975):

$$(6) \quad R_{pc} = \partial C / \partial x * w_d(x)$$

where  $C$  is the concentration of reactive solid phase Mn ("excess Mn") ( $\text{umol cm}^{-3}$ ), and  $w_d(x)$  is the sedimentation rate at depth ( $x$ ) ( $\text{cm yr}^{-1}$ ). The excess Mn pool is mobile and migrates upward to maintain Mn enrichments near the sediment-water interface. Its concentration may be estimated by normalizing the Mn concentration to the Al content, subtracting the mean Mn:Al ratio at depth from all values, and

multiplying by the amount of Al (on a  $\text{cm}^3$  basis):

$$(7) \quad C_s = [(C_{\text{Mn:Al}}(x) - C_{\text{Mn:Al}}(x \rightarrow \infty))] * C_{\text{Al}}(x)$$

where  $C_{\text{Mn:Al}}(x)$  is the Mn:Al ratio at depth  $x$  ( $\mu\text{mol Mn/mg Al}$ ) and  $C_{\text{Al}}(x)$  is the Al concentration ( $\text{mg cm}^{-3}$ ). This provides an estimate of excess Mn in the upper parts of the core. The calculation of  $w_d(x)$  was performed in the following manner:

$$(8) \quad w_d(x) = w_{\text{Al}} * C_{\text{Al}}(x)$$

where  $w_{\text{Al}}$  is the Al sedimentation rate ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ ). A constant flux of Al to the sediment surface is assumed and a changing Al content reflects both changes in porosity and in dilution of the sediment with Mn and Fe oxides (Chapter 4).

The resulting expression for  $R_{\text{pc}}$  is:

$$(9) \quad R_{\text{pc}}(x) = w_{\text{Al}} * \partial C_s / \partial x * C_{\text{Al}}(x)$$

The overall expression for Mn diagenesis is:

$$(10) \quad D_s * \partial^2 C / \partial x^2 + [w_{\text{Al}} * \partial C_s / \partial x * C_{\text{Al}}(x)] = 0$$

Two constants ( $D_s$  and  $w_{\text{Al}}$ ) are found in this expression, and the solution to the equation is constant when the ratio  $D_s:w_{\text{Al}}$  is constant. Thus, a decrease of  $D_s$  by 10% would be equivalent to an increase in the Al sedimentation rate of 10%.

The initial and boundary conditions for this differential equation are the same as used by G.R. Holdren (1977):

$$(11) \quad C(0) = 0.0$$

$$(12) \quad \partial C / \partial x = 0.0 \text{ as } x \rightarrow \infty$$

The basic principles and assumptions implicit in the use of the model may be summarized:

1. Existence of steady state: both the solid phase and pore water profiles are time invariant relative to the sediment-water interface.
2. Advection of pore water is very small and may be neglected. The burial of pore water Mn is less than  $0.1 \text{ umol cm}^{-2} \text{ yr}^{-1}$  whereas the rate of  $\text{Mn}^{2+}$  diffusion is  $>5 \text{ umol cm}^{-2} \text{ yr}^{-1}$ .
3. The sedimentation rate is low, so the effects of adsorption in this system are negligible (Berner, 1976).
4. The influx of Al to the sediments is constant, and the sedimentation rate ( $\text{cm yr}^{-1}$ ) at each depth may be calculated from the Al flux ( $\text{mg cm}^{-2} \text{ yr}^{-1}$ ) and the amount of Al at each depth ( $\text{mg cm}^{-3}$ ).
5. Reactions involving formation of reduced Mn solid phases below the crusts are not considered.
6. Sediment mixing or bioturbation is absent or negligible.
7. The diffusion coefficient is constant at all depths.
8. Horizontal gradients of  $\text{Mn}^{2+}$  and solid phase Mn are negligible relative to the vertical gradients.
9. The pool of redox reactive Mn in these sediments may be estimated by subtracting a non-reactive component which is permanently buried.
10. Total interstitial Mn as determined by AAS is actually  $\text{Mn}^{2+}$ .

It must be emphasized that this model is simply a mass balance model: very little is assumed about the nature of dissolved/solid phase interaction and its main emphasis is on the coupling of phase changes with diffusion. The main value of the model in understanding the chemical aspects of diagenesis comes from an evaluation of the  $R_{pc}$  term. This term gives the total precipitation and dissolution rates in both volume and areal terms, locates the most important zones for phase change reactions and provides insight into the kinetics of dissolution and precipitation.

The solution to this equation was obtained from numerical techniques, because of the great variety of solid phase metal versus depth profiles encountered in the course of the study. The procedure may be outlined:

1.  $C_s(x)$  and  $C_{Al}(x)$  are calculated at all depths
2. Cubic splines or hand drawn curves are derived for each metal or Al profile and  $C_s(x)$  and  $C_{Al}(x)$  are estimated at 0.25 cm intervals.
3.  $\partial C_s(x) / \partial x$  is evaluated numerically from the interpolated  $C_s$  data.
4.  $w_d(x)$  is calculated using a value of  $w_{Al}$  obtained from Pb-210 sedimentation rate estimates and from  $C_{Al}(x)$ .
5.  $R_{pc}(x)$  is calculated at 0.25 cm intervals using equation 6.
6. Equation 10 is solved numerically by finite difference methods (von Rosenberg, 1969) using appropriate values of  $D_s$  and estimated values of  $C$  at 0.0 and 25.0 cm.

7. Different values of  $C(x \rightarrow \infty)$  are run in the model until the boundary condition  $\partial C / \partial x = 0$  as  $x \rightarrow \infty$  is met.

### Manganese Diagenesis

The 8.0 m location on the west transect will be used to demonstrate the application of the model. Excess Mn (Figure 5-7a) reaches concentrations of  $293 \text{ } \mu\text{mol cm}^{-3}$  at 3.7 cm into the core, greatly exceeding the maximum interstitial concentration ( $0.36 \text{ } \mu\text{mol cm}^{-3}$ ). The sedimentation rate in this core is not constant with depth (Figure 5-7b), ranging from  $0.05 \text{ cm yr}^{-1}$  at the interface to  $0.02 \text{ cm yr}^{-1}$  at 10 cm. The  $R_{pc}$  term (equation 9) is plotted in figure 5-7c. Both dissolution and precipitation of Mn oxides occur at substantial rates in this core. Depth integrated reduction and oxidation rates are both approximately  $10 \text{ } \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ .

Molecular diffusion coefficients can be estimated using tracer diffusion coefficients extrapolated to  $4^\circ\text{C}$  (Li and Gregory, 1974;  $D_4 = 111 \text{ cm}^2 \text{ yr}^{-1}$ ) and appropriate corrections for tortuosity (Ullman and Aller, 1982; Lerman, 1979):

$$(13) \quad D_s = D_4 * \phi^2$$

where  $\phi$  is the porosity. Toolik Lake sediment (0-10 cm) has a porosity of 0.95 and a diffusion coefficient of  $100 \text{ cm}^2 \text{ yr}^{-1}$  should be a good estimate.

The pore water Mn profile estimated from this model very closely agrees with the field measurements for this location (Figure 5-7d). A

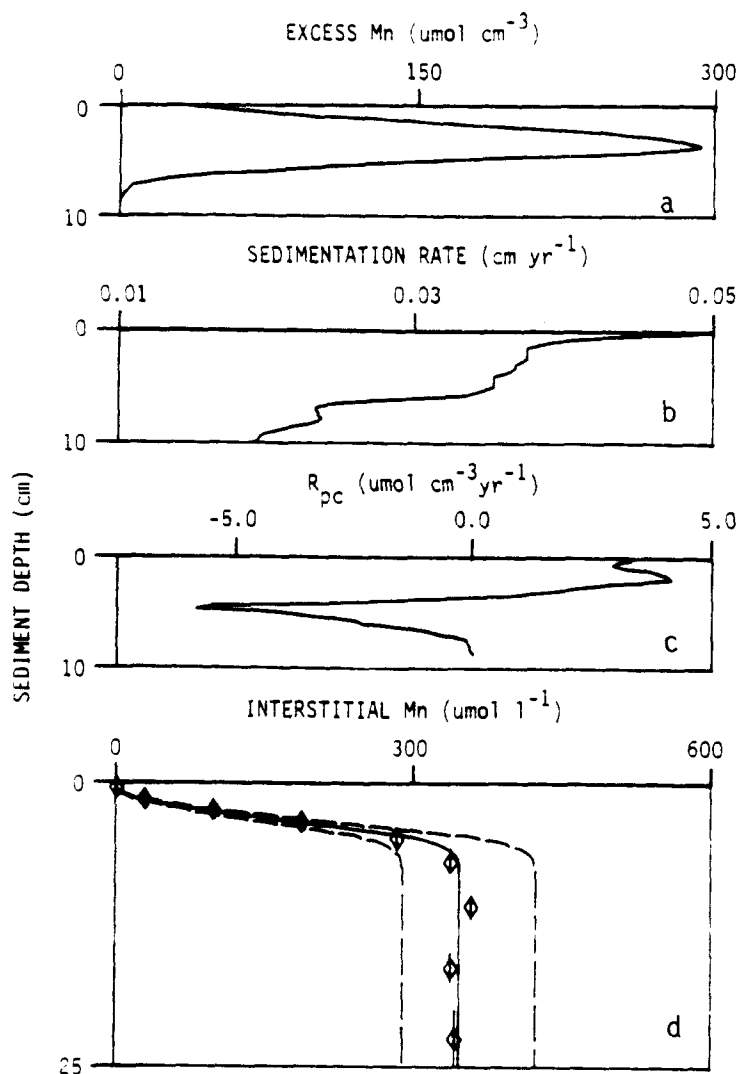


Figure 5-7. Mn model parameters for T80-8.0 core. Plot (a) shows the excess Mn data for the core, (b) shows the depth sedimentation rate as a function of sediment depth, (c) shows the phase change reaction rate, with positive values signifying oxidation, and (d) shows the measured pore water Mn concentration (diamonds), the best fit model output ( $D_s = 95 \text{ cm}^2 \text{yr}^{-1}$ ; solid line) and the dashed lines represent model outputs for  $D_s = 95 \text{ cm}^2 \text{yr}^{-1}$  with sedimentation rate values corresponding to  $\pm 1.0$  SE.



small increase in the sedimentation rate gives the same output as an equivalent decrease in  $D_s$  in this model and results in higher concentrations of Mn in solution.

This model has been applied to six other locations in the lake basin, with fairly good results (Table 5-4). Both T80-5.5 and T80-18.0 fit the model very well in the upper 10 cm of these cores. Core CB80-8.0 does not model very well and other processes (perhaps formation of authigenic Mn(II) minerals) may regulate  $Mn^{2+}$  concentrations. Core T80-3.5 has extremely low concentrations of solid phase Mn and the model does not fit the pore water data. The solid phase profile of Mn in T80-11 exhibits a maximum at the sediment-water interface and the fit is quite good when a  $D_s$  of  $140 \text{ cm}^2 \text{ yr}^{-1}$  is used.

The most Mn-rich core studied (T80-13.0) does not fit the model. The reason for this is not known. Varying  $D_s$  and the sedimentation rate does not result in significant improvement. Non-steady state conditions may exist.

Integration of the  $R_{pc}$  terms with respect to depth yields estimates of the Mn dissolution and precipitation rates on an areal basis (Table 5-4). The 1979 Pb-210 cores were also used for this calculation using Pb-210 sedimentation rates and solid phase Mn profiles. The areal excess Mn is calculated at each of these sites to give an estimate of the diagenetically mobile Mn pool size. From the pool sizes and the Mn reduction rates, the residence time of this excess Mn pool with respect to reduction may be calculated:

Table 5-4. Manganese reaction/diffusion model results.

Core ID	Excess Mn ( $\mu\text{mol cm}^{-2}$ )	Dissolution ( $\mu\text{mol cm}^{-2}\text{yr}^{-1}$ )	Precipitation ( $\mu\text{mol cm}^{-2}\text{yr}^{-1}$ )	Residence Time (yr)	Model Fit	Best $D_s$ ( $\text{cm}^2\text{yr}^{-1}$ )	Highest Mn ( $\text{mg g}^{-1}$ )
T80- 3.5	4.3	0.02	0.	38	poor	-----	1.2
T80- 5.5	63.	2.4	0.	26	good	100	21.
T80- 8.0	1020.	9.5	10.4	107	good	95	135.
T80- 11.0	898.	13.7	0.	66	good	140	149.
T80- 13.0	1410.	15.1	15.0	93	poor	-----	169.
T80- 18.0	668.	15.1	12.9	44	good	140	154.
CB80- 8.0	4.4	0.12	0.	37	poor	-----	1.3
T79A- 5.5	0.9	0.04	0.	22	----	-----	0.5
T79C- 6.0	94.	9.9	0.	9	----	-----	38.
T79D-10.0	1.0	0.03	0.	32	----	-----	0.5
T79E- 7.5	449.	5.1	4.9	88	----	-----	66.
T79F- 7.0	357.	6.5	4.4	55	----	-----	57.
T79G- 6.0	2.5	0.12	0.	21	----	-----	1.3

$$(14) \quad T_d = (\int C_s(x) dx) / (\int R_d(x) dx)$$

where  $T_d$  is the residence time of excess Mn with respect to dissolution (yr),  $C_s$  is the excess solid phase Mn ( $\mu\text{mol cm}^{-3}$ ) and  $R_d$  is the dissolution rate of solid phase Mn ( $\mu\text{mol cm}^{-3} \text{ yr}^{-1}$ ). It must be emphasized that this residence time is not the residence time of excess Mn in the sediment. It is the residence time only with respect to dissolution processes. In cores in which the precipitation rate is approximately equal to the dissolution rate, most or all of this excess Mn is retained by the sediment. Flux of  $\text{Mn}^{2+}$  through the sediment-water interface occurs when dissolution exceeds precipitation. Oxidation at or just above the interface may also result in retention of this diffusing  $\text{Mn}^{2+}$  at the sediment-water interface.

The Mn residence time estimates span one order of magnitude (Table 5-4), averaging  $49 \pm 30$  yr. The shortest residence time of 9 yr occurs at T79C-6.0, the fastest sedimentation location sampled. Residence times of excess Mn may be useful parameters for the comparison of Mn diagenesis in different sediment environments. Sediments with reducing conditions near the interface should have very low Mn residence times.

These 12 cores present wide ranges in the amounts of excess depth integrated Mn and rates of Mn flux. Five of these cores have very low concentrations of excess Mn ( $<5 \mu\text{mol cm}^{-2}$ ), two have intermediate amounts ( $5\text{--}100 \mu\text{mol cm}^{-2}$ ) and six cores have high concentrations ( $>100 \mu\text{mol cm}^{-2}$ ).

Toolik Lake has the highest concentrations of Mn within accumulating sediment of any environment studied (Table 5-5). High Mn concentrations ( $\text{mg g}^{-1}$ ) are found in marine pelagic sediments (Froelich et. al., 1979; and others), in sediments from the Gulf of Mexico (Trefry and Presley, 1982), and in the littoral sediment of Feldsee (Tessenow and Baynes, 1978). The work of Froelich et. al. (1979) and Burdige and Gieskes (1983) has shown that the diagenetic remobilization of Mn in marine pelagic sediments results in layers of Mn oxides accumulating below the sediment-water interface. Trefry and Presley (1982) have shown that the diagenetic reduction/diffusion/oxidation mechanism can result in Mn enrichments within sediments, the remobilization of Mn from reducing Mississippi Delta sediments (fluxes up to  $15 \text{ umol cm}^{-2} \text{ yr}^{-1}$ ) and the enrichment of the more oxidizing pelagic sediments as a consequence.

Tessenow and Baynes (1978) found high concentrations of Mn accumulating below the roots of aquatic plants resulting from the oxidizing conditions found in the root zone. This lacustrine Mn accumulation mechanism is analagous to Toolik Lake, with Mn and Fe becoming separated into distinct zones. I have estimated a dissolution rate for Feldsee by assuming that Mn diffusion is equal to the rate of dissolution and precipitation. The rate is similar to that found in Toolik Lake sediment and the residence time should be similar.

The examples here fall into two categories: those in which oxidizing conditions are found below the sediment-water interface; and

Table 5-5. Manganese fluxes in aquatic sediments.

Location	Excess Mn ( $\mu\text{mol cm}^{-2}$ )	Dissolution Rate ( $\mu\text{mol cm}^{-2} \text{yr}^{-1}$ )	Residence Time (yr)	$D_s$ ( $\text{cm}^2 \text{yr}^{-1}$ )	Maximum Mn ( $\text{mg g}^{-1}$ )	References
Atlantic Ocean	70	0.3 <sup>a</sup>	250	72	20.	A
Long Island Sound	2-7	21-168 <sup>a</sup>	0.04-0.12	62-105	1.	B
Mississippi Delta	-----	0-15 <sup>a</sup>	-----	80-130	12.5	C
Esthwaite Water	-----	3.3 <sup>a</sup>	1	-----	-----	D
Lake Vechten	-----	16. <sup>b</sup>	-----	-----	-----	E
Narragansett Bay	-----	7-18 <sup>c</sup>	-----	-----	-----	F
Experimental Lakes	-----	0.4-1.2 <sup>b,d</sup>	-----	-----	1.	G
Lake Michigan	4	0.2 <sup>a</sup>	20	28	1.	H
Feldsee	-----	7. <sup>e</sup>	-----	-----	68.	I
Toolik Lake	1-1410	0.02-15.1 <sup>a</sup>	10-110	95-140	169.	This study.

- a. Dissolution of solid phase Mn.  
b. Anoxic hypolimnion accumulation.  
c. Flux chamber experiments.  
d. Summer flux only.  
e. From pore water gradient.

- A. Froelich et al., 1979; Burdige & Gieskes, 1983  
B. Aller, 1980b  
C. Trefry & Presley, 1982  
D. Davison et al., 1982  
E. Verdouw & Dekkers, 1980  
F. McCaffrey et al., 1980  
G. Kelley et al., 1982; Brunskill et al., 1971  
H. Robbins & Callender, 1975  
I. Tessenow & Baynes, 1978

those in which oxidizing conditions are found at and above the sediment-water interface. The more oxidized systems can retain Mn very effectively because of oxidation of Mn within the sediment. Pelagic marine sediments, Feldsee sediments and profundal Toolik Lake sediments are the only examples from Table 5-4 in which Mn solid phase concentration maxima are found below the sediment-water interface. At the other extreme are environments with short Mn residence times which result from anoxic water columns or reducing sediments. Among these are Long Island Sound, Esthwaite Water, Lake Vechten, Narragansett Bay and the Experimental Lakes Area. Lake Michigan is an intermediate case.

From this modelling exercise, several conclusions about Mn diagenesis in Toolik Lake can be drawn:

1. A steady state diagenetic model using terms for diffusion and precipitation/dissolution can explain the observed  $\text{Mn}^{2+}$  distribution.
2. In general, fluxes of  $\text{Mn}^{2+}$  within littoral zone sediments are less than profundal zone sediments because of the higher concentrations of solid phase Mn within profundal sediments.
3. Despite very low sedimentation rates, the dissolution rate of Mn ( $\text{umol cm}^{-2} \text{ yr}^{-1}$ ) is similar to that found in some more reducing sediments.
4. Only pelagic oceanic, continental slope and Feldsee sediments have sediment Mn cycles similar to those in Toolik Lake. These sediments have oxic conditions within surficial sediments.

## Iron Diagenesis

The application of the model to Fe diagenesis is more difficult than for Mn diagenesis. The chief difficulty arises in the estimation of the solid phase diagenetic Fe concentrations because of the existence of multiple Fe concentration peaks; subjective choices of excess Fe concentrations must be made. In the cores with Mn crusts, the first large peak in Fe concentration is considered to be the mobile Fe pool, although that Fe(III) reduction most likely occurs over a much wider zone.

Figure 5-8a shows excess Mn and Fe for core T80-18.0. The Fe crust lies immediately below the Mn crust. The  $R_{pc}$  terms for both Mn and Fe (Figure 5-8b) indicate that Mn reduction and Fe oxidation occur in approximately the same region, with similar rates of reaction. The model predicts  $Fe^{2+}$  concentrations quite well (Figure 5-8c) when the estimated  $D_s$  of  $111 \text{ cm}^2 \text{ yr}^{-1}$  is used (using equations from Ullman and Aller (1982) and Li and Gregory (1974)).

As in the case for Mn diagenesis, a reduction/diffusion/oxidation mechanism effectively describes the observed distribution of Fe in porewater and sediment. Table 5-6 shows the model results for all cores. The concentrations of excess Fe are probably known to approximately  $\pm 25$  to 50% due to difficulties in estimating diagenetic Fe(III). Iron dissolution rates are generally similar to Mn dissolution rates and 7 out of the 13 cores examined had high rates of Fe oxidation within the sediment.

The model produces an  $Fe^{2+}$  profile similar to the measured

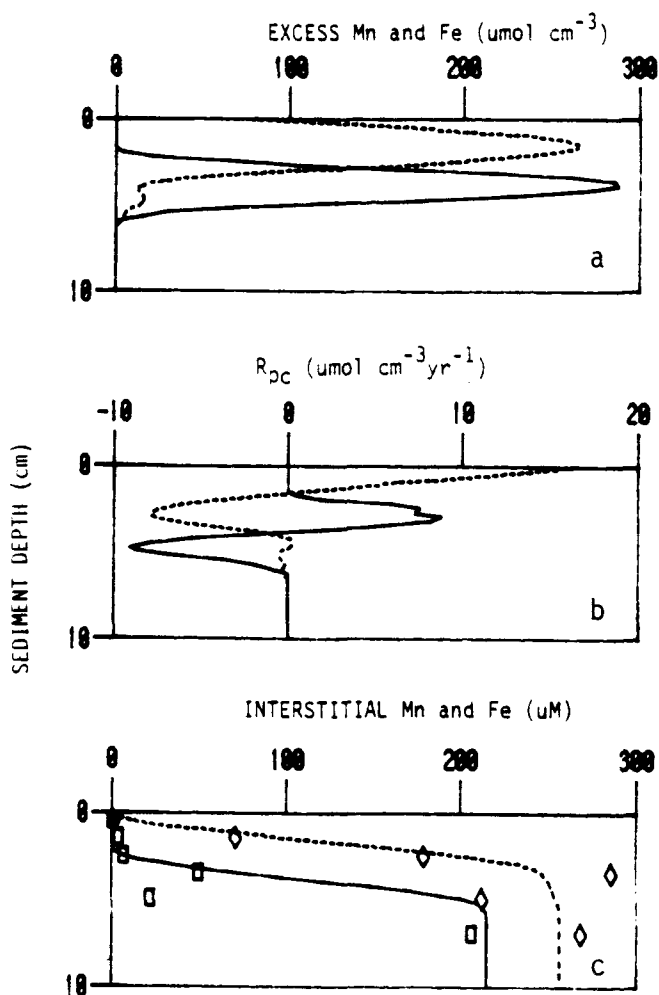


Figure 5-8. Mn and Fe model output for the 18.0 m station. Plot (a) shows the excess Mn and Fe concentrations; (b) shows the dissolution and precipitation rates; and (c) shows the model output and pore water data for this core. Solid lines are Fe model output, dashed lines are Mn model output, rectangles are pore water Fe concentrations and diamonds are pore water Mn concentrations.



Table 5-6. Iron reaction/diffusion model results.

Core ID	Excess Fe ( $\mu\text{mol cm}^{-2}$ )	Dissolution ( $\mu\text{mol cm}^{-2}\text{yr}^{-1}$ )	Precipitation ( $\mu\text{mol cm}^{-2}\text{yr}^{-1}$ )	Residence Time (yr)	Model Fit	Best $D_s$ ( $\text{cm}^2\text{yr}^{-1}$ )	Highest Fe ( $\text{mg g}^{-1}$ )
T80- 3.5	250	0.7	0.	357	poor	-----	48
T80- 5.5	900	13.5	0.	67	good	50	180
T80- 8.0	400	3.9	3.9	102	good	60	133
T80- 11.0	1200	8.4	8.4	143	poor	150	178
T80- 13.0	500	3.9	3.9	128	good	110	162
T80- 18.0	400	13.4	13.4	30	good	110	182
CB80- 8.0	200	5.7	0.	35	poor	-----	73
T79A- 5.5	25	1.0	0.	25	----	-----	24
T79C- 6.0	700	30.	5.	23	----	-----	167
T79D-10.0	100	2.5	0.	40	----	-----	48
T79E- 7.5	1200	18.	18.	67	----	-----	223
T79F- 7.0	1000	20.	20.	50	----	-----	214
T79G- 6.0	100	5.	0.	20	----	-----	76

profile in four out of seven cores. Low  $D_s$ 's were used in two of these cores suggesting that tortuosity is higher in these cores or that the estimated rates of Fe reduction and oxidation underestimate the true rates. Two out of the three cores with poor fits occur in locations where the Mn model fit was poor. Iron residence times averaged  $87 \pm 89$  years, and the shortest residence times (20 and 23 yr) occur in the locations with the fastest accumulation rates.

There are few studies of Fe diagenesis directly applicable to the formation of Fe crusts (Table 5-7), with the work of Tessenow and Baynes (1975; 1978) being similar to this study. Feldsee sediments have high concentrations of diagenetic Fe and Mn under aquatic plants, and the rates of Fe dissolution and precipitation are in the same range as this study. Aller (1980b) estimated Fe flux from the solid phase Fe profile in anoxic Long Island Sound sediments and found rates much greater than in Toolik Lake. The remaining three studies are from anoxic basins and produce rates similar to the highest rates found in Toolik Lake. Despite sedimentation rates that are lower than other systems, Toolik Lake has comparable rates of Fe dissolution, suggesting that organic matter oxidation in Toolik Lake depends upon the reduction of metals to a greater extent than in these other systems.

The results of the application of this model to Fe diagenesis may be summarized:

1. A reduction/diffusion/oxidation mechanism of crust formation is the cause of Fe enrichments in these sediments, in agreement with the

Table 5-7. Iron fluxes in aquatic sediments.

Location	Excess Fe ( $\mu\text{mol cm}^{-2}$ )	Dissolution Rate ( $\mu\text{mol cm}^{-2} \text{yr}^{-1}$ )	Residence Time (yr)	$D_s$ ( $\text{cm}^2 \text{yr}^{-1}$ )	Maximum Fe ( $\text{mg g}^{-1}$ )	References
Long Island Sound	40-100	250-1200 <sup>a</sup>	0.07-0.16	67-161	30	A
Estwaite Water	-----	30 <sup>b</sup>	-----	-----	--	B
Lake Vechten	-----	25 <sup>c</sup>	-----	-----	--	C
Experimental Lakes	-----	5-16 <sup>c</sup>	-----	-----	40	D
Feldsee	-----	7 <sup>d</sup>	-----	-----	123	E
Toolik Lake	25-1200	1-30 <sup>a</sup>	25-360	50-150	223	This study.

- a. Dissolution of solid phase Fe.  
b. Sediment traps and mass balance.  
c. Anoxic hypolimnion accumulation.  
d. From pore water gradient.

- A. Aller, 1980  
B. Davison et al., 1982  
C. Verdouw and Dekkers, 1980  
D. Kelley et al., 1982; Brunskill et al., 1971  
E. Tessenow and Baynes, 1978

experimental results of Carignan and Flett (1981).

2. The dissolution rates of solid phase Fe per  $\text{cm}^2$  is high throughout the lake, with no strong relationship to lake depth. These rates are comparable to those found elsewhere.

### PHOSPHORUS DIAGENESIS

Figure 5-9 shows profiles of the solid phase P:Al ratio and the pore water  $\text{PO}_4$  concentrations. The largest increases in  $\text{PO}_4$  concentrations occur below the highest solid phase P concentrations, similar to the distribution of solid and pore water Fe and Mn. Attempts to model P diagenesis with the diffusion/reaction model fail because:

1. Multiple P concentration peaks and relatively small P enrichments in some cores make estimation of excess P impossible.
2. There is much scatter in the pore water  $\text{PO}_4$  data.
3. Removal of  $\text{PO}_4$  as Mn(II)-Fe(II) phosphates is occurring in many of these sediment cores, and the model does not include terms for this process.

Despite these problems, it is clear that the large P enrichment found at or below the Fe rich horizon results from diagenetic processes such as those proposed by Carignan and Flett (1981). The association of P with Fe in these sediments has two components: adsorbed P (Prentki, 1975) and discrete metal phosphates (Tessenow, 1974). An important question about the diagenesis of P is whether the large P enrichments are a result of discrete P mineral formation or an adsorbed complex. Figure 5-9 shows the distribution of solid phase P on an Al basis for two cores. The section in which vivianite becomes saturated or supersaturated is shown for each case, and sections where vivianite nodules were found (by visual inspection) are indicated. Vivianite becomes saturated below the highest solid phase P concentration horizons. Vivianite cannot account for the P rich horizon.

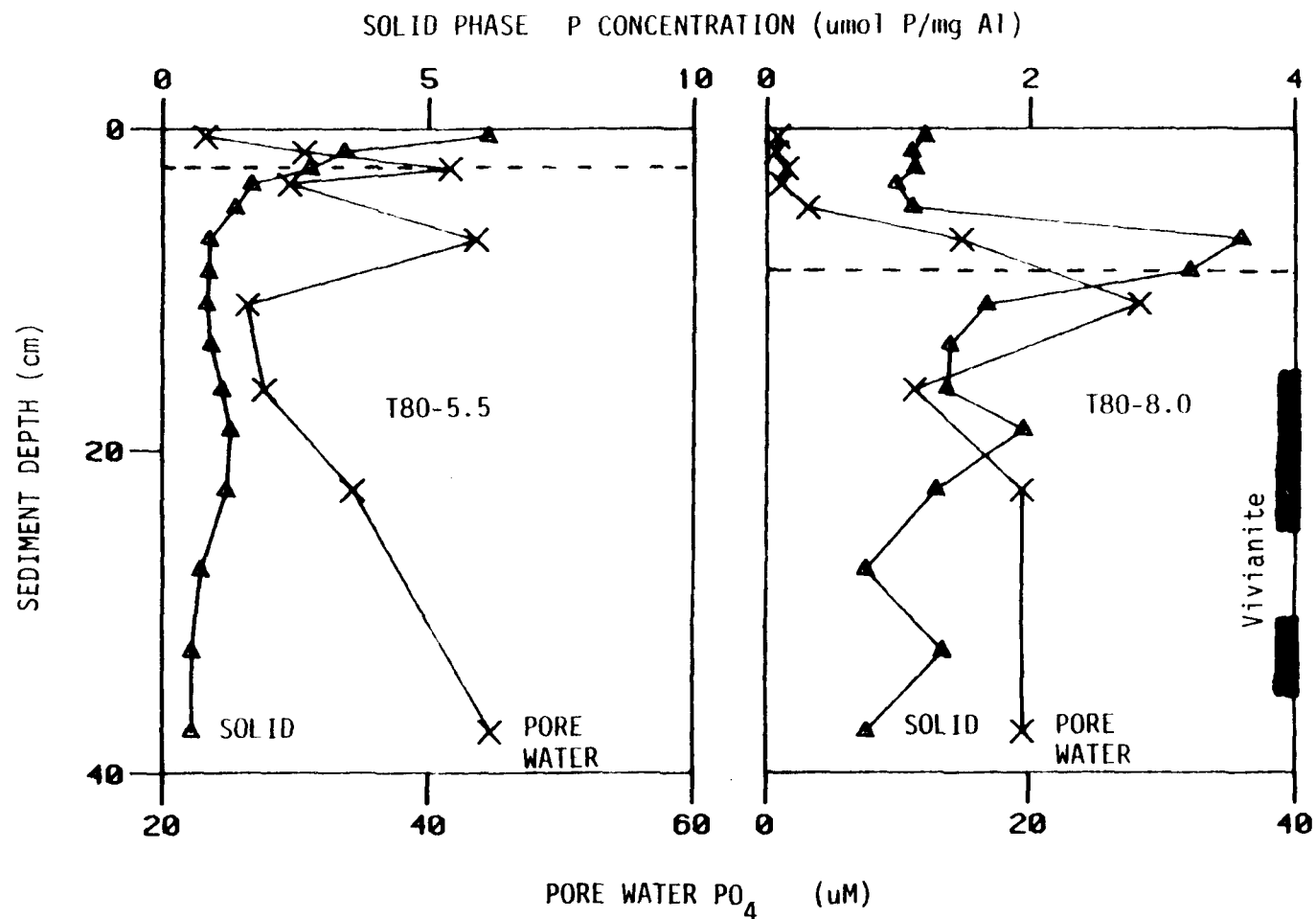


Figure 5-9. Solid phase and interstitial P concentrations for two cores. The solid phase data has been normalized to the Al concentration. The horizontal dotted line corresponds to the beginning of the vivianite saturation zone (saturation exists below the line). Depths at which vivianite was found via visual inspection are indicated with a vertical line.

Adsorptive and authigenic mineral forming modes of Fe-P association are occurring in these sediments. The following reaction sequence may be hypothesized:

1. Organic and inorganic P is sedimented from the water column.
2. The sedimented inorganic P and remineralized organic P become associated with Fe(III) oxyhydroxides which are abundant in surficial sediments.
3. As more sediment accumulates, this Fe(III)-inorganic P complex is buried, eventually encountering conditions suitable for Fe(III) reduction.
4. As solid phase Fe(III) is reduced to aqueous Fe(II), phosphate is released to the interstitial solution, and it diffuses either upward towards more oxidized conditions where P adsorbs to Fe(III) again, or downward to be precipitated as Fe(II)-Mn(II) phosphates.
5. These migrations result in the formation of P-rich horizons at a point above where the Fe(III) complex dissolves. It is the concentrating of P in this horizon which results in elevated interstitial phosphate concentrations below this depth.

This fifth step creates conditions suitable for the precipitation of vivianite and/or Fe(II)-Mn(II) phosphates. High concentrations of pore water  $\text{Fe}^{2+}$  from the reduction/diffusion/oxidation mechanism and the apparent absence of Fe(II) carbonate or sulfide precipitation results in the formation of these phosphate minerals. High  $\text{Fe}^{2+}:\text{PO}_4$  and  $\text{Mn}^{2+}:\text{PO}_4$  ratios in pore water result in  $\text{PO}_4$  concentrations that are largely controlled by formation of authigenic metal phosphates.

### LIMITATIONS OF THE MODEL

Several limitations in the use of the mass balance model have been found in its applications to Mn and Fe diagenesis. One problem has been the relatively poor resolution of the solid phase Mn and Fe data because of 1.0 cm and larger sampling intervals. In the case of Mn oxidation in the upper part of several cores, the calculation of the shape of the oxidation rate profile relies upon only one through three sediment sections. Caution must be exercised when examining the shape and magnitude of Mn oxidation profiles. Sampling resolution is even more of a problem for Fe oxidation and reduction because the Fe crusts may be less than one centimeter in thickness. Both oxidation and reduction profiles associated with Fe crusts depend heavily upon the curve drawn through relatively few solid phase Fe data points.

The estimation of diagenetically mobile Fe and Mn can be subjective, especially for Fe. Multiple peaks of solid phase Fe concentration throughout the cores represent large amounts of Fe which are assumed to be diagenetically immobile. The diagenesis of Fe crusts may not be a steady state process, and the capacity of the sediment to reduce Fe(III) may vary with time because of variable inputs of electron donors. Distinguishing between diagenetically mobile Fe and other non-mobile forms is difficult because the solid phase Fe content is very high throughout these cores, and one cannot subtract a background value as simply as for Mn. Despite these limitations, the model indicates that Mn and Fe enrichments in oxidized zones result from a reduction/diffusion/oxidation cycle which maintains metal rich



zones stationary relative to the sediment-water interface.

#### METAL OXIDATION AND REDUCTION RATES: GEOCHEMICAL IMPLICATIONS

The oxidation and reduction of Mn in aquatic sediments and in natural waters has been a topic of interest in recent years. Manganese oxidation can proceed via microbially mediated pathways (Chapnick *et al.*, 1982; Emerson *et al.*, 1982; Burdige, 1983) or by inorganic reactions (Morgan, 1967). The same is true for Mn reduction (Burdige, 1983; Watanabe and Furasaka, 1980). When these processes are modelled in sediments, first order reactions are usually assumed (Burdige and Gieskes, 1983; G.R. Holdren, 1977). This study of Mn and Fe oxidation and reduction examines whether first order models are applicable and yields kinetic constants which may be compared with those from other environments.

#### Manganese Reduction

The reduction of Mn has been discussed by Burdige and Gieskes (1983) for the case of pelagic marine sediments. They assume that Mn reduction may be treated as a first order process, where the rate of dissolution is proportional to the surface area of dissolving solid phase Mn:

$$(15) \quad d C_s / dt = K_{red} * C_s$$

The solution to equation 15 is simply:

$$(16) \quad \ln C_s = \ln C_s(0) - (K_{red} * t)$$

The dissolution rate constant  $K_{red}$  may be evaluated from a plot of  $C_s$  versus time (Figure 5-10). The time scale was computed for each core using the Pb-210 sedimentation rate. Excess Mn concentrations in the portions of the cores where Mn content decreases with increasing depth are used for this plot.

The first order kinetic model fits T80-13 and T79A-55 quite well (Figure 5-10) but not the other cores. Plots of  $\log C_s$  versus time exhibit changing slopes within a given core. The absence of linear fits to the first order model (Figure 5-10) may result from changes in the chemical environment or an improper assumption of steady state.

Table 5-8 presents the reduction constants found in this study and in three other studies. It should be noted that the  $K$ 's calculated for Toolik Lake are approximate, and represent a mean value for a core. The range for Toolik Lake cores ( $0.006$  to  $0.057 \text{ yr}^{-1}$ ) encompasses Holdren's (1977) value for Chesapeake Bay and is higher than that found for pelagic marine sediments (Burdige and Gieskes, 1983). Long Island Sound sediments have vastly greater reduction rate constants (Aller, 1980b).

Manganese(IV) reduction in freshwater and marine sediments can result from biogenic or inorganic reactions. Stone (1983) has shown that a number of organic substances can reduce Mn oxides. Marine and freshwater bacteria can reduce Mn oxides when bacterial cells are closely associated with Mn oxides (Ehrlich, 1981). The production of reduced metabolic products by bacteria may also provide an indirect method of Mn(IV) reduction. Reduced sulfur compounds reduce soil

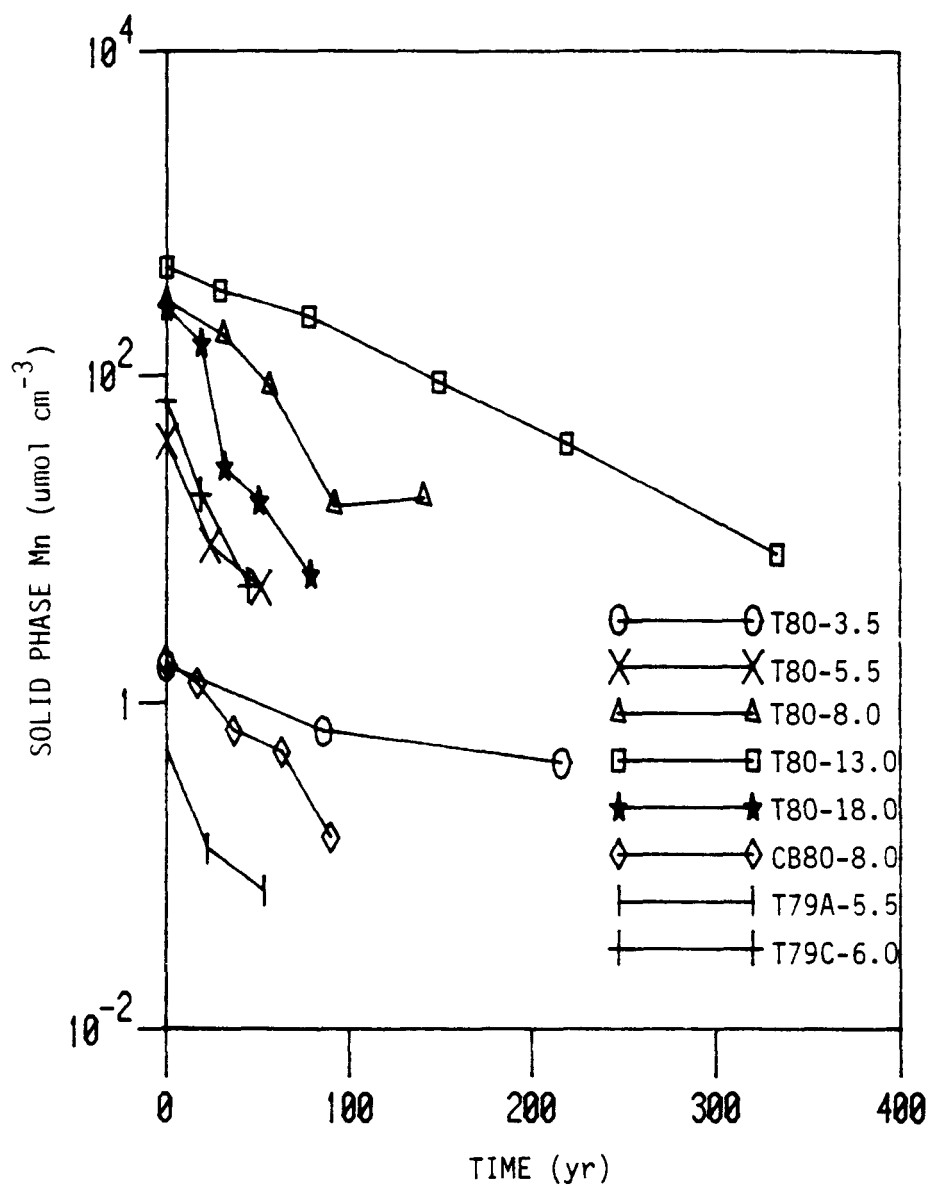


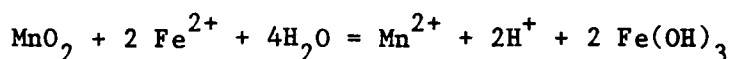
Figure 5-10. First order dissolution of Mn. The log of the solid phase Mn concentration (from below the crusts and enriched zones) is plotted versus the Pb-210 derived times, taking the Mn maximum as time zero.

Table 5-8. Reduction of manganese and iron; first order kinetic constants. All data are expressed as  $\text{yr}^{-1}$ .

Location	Manganese	Iron	References
T80- 3.5	0.006	0.003	This study.
T80- 5.5	0.039	0.007	" "
T80- 8.0	0.031	0.048	" "
T80- 13.0	0.012	-	" "
T80- 18.0	0.050	-	" "
CB80- 8.0	0.026	0.019	" "
T79A- 5.5	0.036	0.031	" "
T79C- 6.0	0.057	0.071	" "
Chesapeake Bay	0.017	-	G. R. Holdren, 1977
Long Island Sound	8.2-25.0	-	Aller, 1980b
Pelagic Atlantic	0.002	-	Burdige & Gieskes, 1983

Mn(IV) (Ehrlich, 1981) and studies indicate that reduction of Mn(IV) can result from the microbial production of sulfide (Burdige, 1983).

In Toolik Lake sediment, Mn reduction often occurs in the presence of high  $\text{Fe}^{2+}$  concentrations and the following reaction may occur:



From the thermodynamic constants for Mn(IV)-Mn(II) and Fe(III)-Fe(II) half reactions (Stumm and Morgan, 1981), it is possible to estimate the  $\text{Fe}^{2+}$  concentration when pH and the  $\text{Mn}^{2+}$  concentration are known:

$$(17) \log(a_{\text{Fe}^{2+}}) = 0.5 * \log(a_{\text{Mn}^{2+}}) - \text{pH} - 4.7$$

At a pH of 7.0 and a  $\text{Mn}^{2+}$  activity of 10.0  $\mu\text{M}$ ,  $6.3 * 10^{-15} \text{ M}$   $\text{Fe}^{2+}$  is in equilibrium. Higher concentrations of  $\text{Fe}^{2+}$  at the bottom of the Mn rich horizons can reduce great quantities of Mn(IV).

To examine whether  $\text{Fe}^{2+}$  concentrations affect the rate constant for  $\text{MnO}_2$  reduction, the  $K_{\text{red}}$  values were plotted as a function of the maximum  $\text{Fe}^{2+}$  concentration found in each core (Figure 5-11). Both the highest and the lowest  $K_{\text{red}}$  values for each core were plotted and although the range was quite large, the overall pattern suggests that cores with higher  $\text{Fe}^{2+}$  concentrations in interstitial solution have larger Mn reduction rate constants. This conclusion must be viewed with caution because:

1. The concentration of  $\text{Fe}^{2+}$  varies greatly in the horizons where

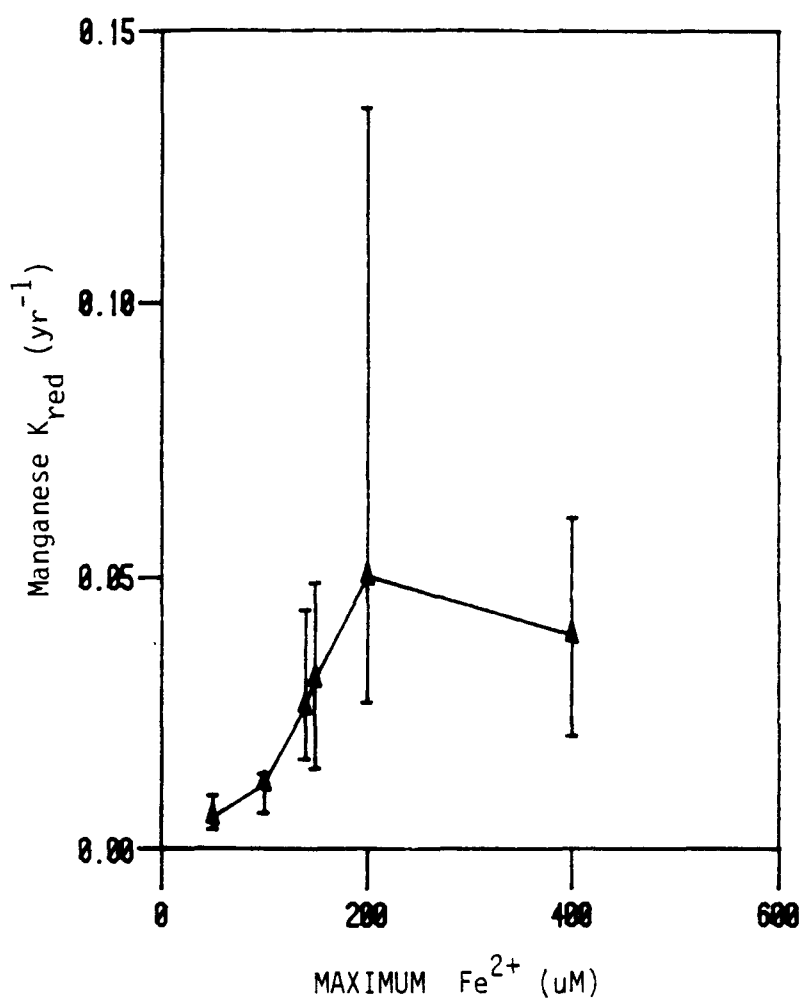


Figure 5-11. The Mn dissolution  $K$ 's are plotted versus the concentration of pore water Fe in each core. The Fe data were taken just below the region of Mn dissolution. The error bars show the maximum and minimum  $K$ 's obtainable from adjacent points in Figure 5-10.

Mn(IV) is being reduced, and the  $\text{Fe}^{2+}$  concentrations where Mn(IV) oxides are being reduced are not known.

2. Both high  $\text{Fe}^{2+}$  concentrations and rapid Mn reduction may result from the same processes within sediments.

3. The chemical and physical characteristics of solid phase Mn may not be constant throughout these cores.

In view of the favorable thermodynamic situation, it is likely that Mn(IV) reduction via  $\text{Fe}^{2+}$  oxidation occurs to some extent in Toolik Lake sediments. Stoichiometry predicts that the reduction of one mole of Mn(IV) requires the oxidation of two moles of Fe(II).

Watanabe and Furusaka (1980) have cited work by Yoshida and Kamura (1975) which suggests that Mn(IV) was chemically reduced by Fe(II) in rice paddy soils. In general, this coupling of Mn reduction with Fe oxidation has not been examined or observed in aquatic sediments.

The oxidation state of natural and synthetic Mn oxides is often less than 4.0, with fresh precipitates being less than 3.0 (Hem, 1980). Using data from Hem (1980, Figure 3), the predicted oxidation state of Mn is between 2.7 and 3.0 at a pH of 7.0 and with  $\text{Mn}^{2+}$  concentrations between 10 and 100  $\mu\text{M}$ . At a lower pH of 6.4, the oxidation state would be between 3.25 and 3.99, suggesting that the reduction of Mn oxides to  $\text{Mn}^{2+}$  in Toolik Lake sediment requires between one and two electrons. At lower oxidation states, less  $\text{Fe}^{2+}$  would be required to reduce Mn oxides to  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$  oxidation could account for a higher proportion of Mn reduction.

The rapid change in chemical environment found in the zone of Mn reduction probably is one of the main reasons that simple first order kinetic models are not applicable to all of these profiles. Much of the Mn reduction occurs in a zone where pE can change by up to five units and pH can change by one unit, with  $\text{Fe}^{2+}$  concentrations varying by several orders of magnitude. The chemistry of the Mn oxide-solution interface may change because of formation of Fe(III) oxide precipitates and the reduction of these Fe oxides below the Fe oxidizing zone.

#### Iron Reduction

Iron(III) reduction mechanisms in aquatic sediments may have inorganic and microbiological components (Sorenson, 1982). Organic acids and sulfide may be the prime agents of Fe(III) reduction. Sorenson (1982) others have shown that facultatively anaerobic bacteria may be responsible for microbial reduction.

The first order approximation of Fe(III) reduction appears to be useful for some cores (Figure 5-12). The  $K_{\text{red}}$  values for Fe dissolution are quite similar to those for Mn reduction.

#### Manganese Oxidation

The oxidation of Mn in natural waters can proceed abiotically (Morgan, 1967; Hem, 1981; Stumm and Morgan, 1981) or with biological mediation (Chapnick et al., 1982; Emerson et al., 1982; Ehrlich, 1981). Morgan (1967) has shown that the chemical oxidation of Mn(II) follows the rate law:



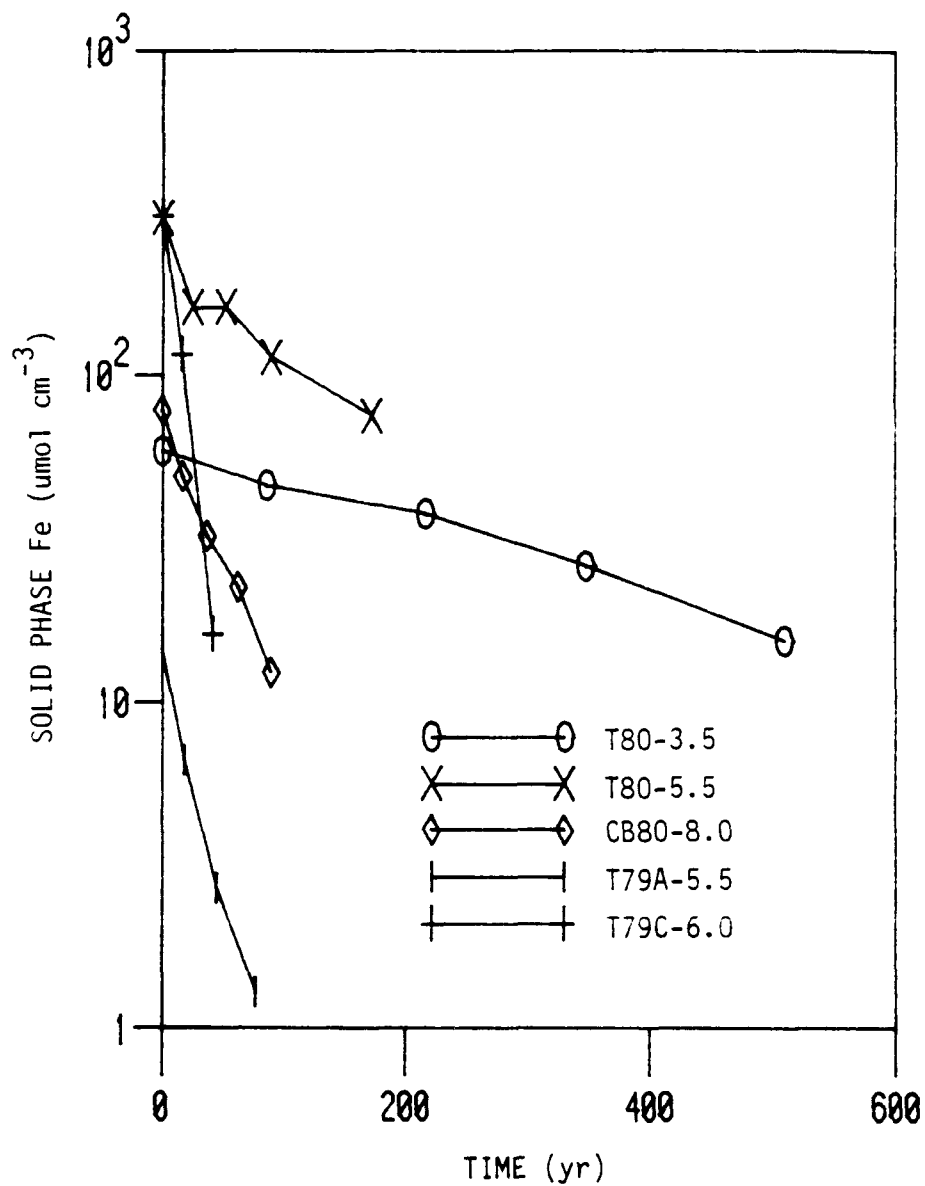


Figure 5-12. First order dissolution of Fe. The log of the solid phase Fe concentration (from below the crusts and enriched zones) is plotted versus Pb-210 derived times, taking the Fe maximum as time zero.

$$(18) \quad -d [\text{Mn}^{2+}]/dt = K_{\text{ox1}} * [\text{Mn}^{2+}] + K_{\text{ox2}} * [\text{Mn}^{2+}][\text{MnO}_x]$$

where  $K_{\text{ox1}}$  and  $K_{\text{ox2}}$  are constants and  $[\text{MnO}_x]$  is the concentration of solid phase Mn. This is an autocatalytic reaction which holds for constant pH and  $p\text{O}_2$  (oxygen partial pressure), and the  $K_{\text{ox}}$  values vary with changes in temperature, pH and  $p\text{O}_2$ . The term  $[\text{MnO}_x]$  may be replaced by a surface area term (Hem, 1981). Removal of  $\text{Mn}^{2+}$  from solution initially results in the formation of oxides with an oxidation state near 3.0, with higher oxidation states occurring with aging (Hem, 1981). The oxidation of  $\text{Mn}^{2+}$  may be treated as a pseudo first order reaction when there is a large Mn oxide surface area (Hem, 1981). The loss of  $\text{Mn}^{2+}$  from solution was examined in T80-8.0, a core in which the solid phase Mn maximum occurs approximately 3.7 cm below the sediment-water interface. Since advection is low in these sediments, an equation may be written in which only diffusion and first order oxidation occur:

$$(19) \quad D_s \partial C / \partial x - K_{\text{ox}} * C = 0.0$$

This equation is solved for the boundary conditions  $C(L) = 0.0$  and  $C(0) = \text{CEQ}$  where CEQ is the concentration of  $\text{Mn}^{2+}$  at the point of maximum solid phase Mn concentration, and L is the distance in cm between  $C(0)$  and the point where the concentration of  $\text{Mn}^{2+}$  is zero. Figure 5-13 shows its application to the data for T80-8.0, with  $L = 2.5$  cm,  $\text{CEQ} = 188 \text{ } \mu\text{M Mn}^{2+}$  and  $K_{\text{ox}} = 25 \text{ yr}^{-1}$ . The other cores are not amenable to this treatment because the oxidation of  $\text{Mn}^{2+}$  occurs over too small

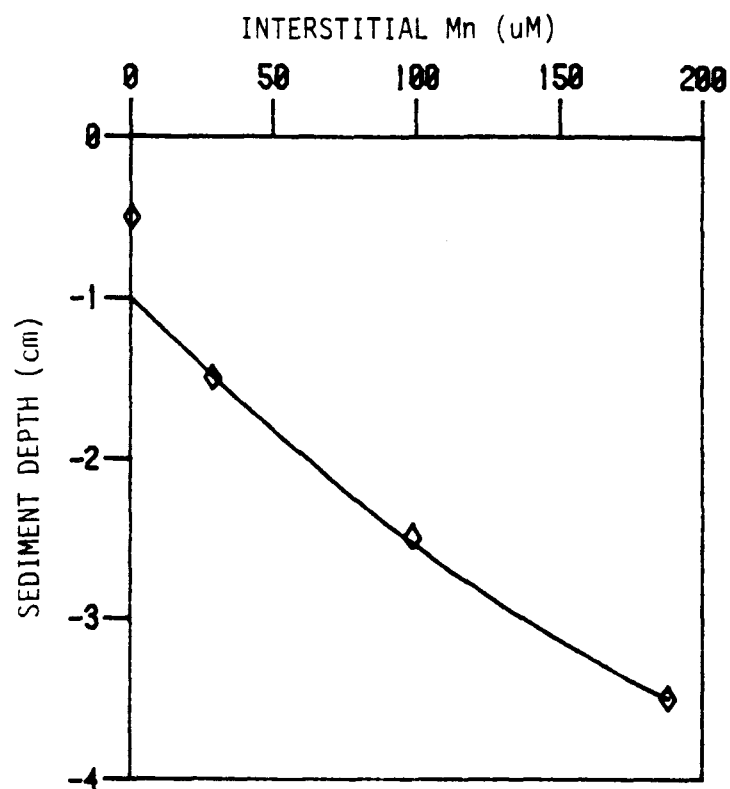


Figure 5-13. A plot of interstitial water data and model output for first order removal of Mn from solution. The best fit is for  $K = 25 \text{ yr}^{-1}$ . See text for details.

a depth interval.

Similar first order constants have been derived from other sediment and water column environments. Burdige and Gieskes (1983) estimate values of  $12 \text{ yr}^{-1}$  for pelagic marine sediments, and cite laboratory rates from Aller for Long Island Sound sediment approximately  $50 \text{ yr}^{-1}$ . Emerson et al. (1979) found rates of  $180 \text{ yr}^{-1}$  for the Saanich Inlet water column, a result of microbial Mn oxidation (Emerson et al., 1982).

Comparison of the rates of Mn oxidation observed in Toolik Lake sediments to laboratory studies of abiotic Mn oxidation may not be valid because most studies are run at pH's greater than those observed in this study. Other unknown parameters which hinder comparison to other studies are the the oxygen partial pressure and the Mn oxide surface area available for autocatalysis. From other studies, it is clear that the large concentrations of solid phase Mn should enhance chemical Mn oxidation (Hem, 1981).

The importance of microbial Mn oxidation in some aquatic environments has been demonstrated by several other investigators (Emerson et al., 1982; Chapnick et al., 1982; Ehrlich, 1981). In Toolik Lake sediment, the extent of microbial participation in the oxidation of Mn is unknown. Chapnick et al. (1982) found that microbial Mn oxidation was inhibited by  $\text{Mn}^{2+}$  concentrations  $> 20 \text{ uM}$  and if Toolik Lake sediment behaved similarly, the microbial component of Mn oxidation may be restricted to a small zone near the sediment-water interface.

If Mn binding and oxidation were strictly a first order process

then the maximum rates of Mn binding would occur where  $\text{Mn}^{2+}$  concentrations were high, assuming that the solid phase Mn surface area was constant. Because this oxide surface area decreases as the sediment-water interface is approached from below, the rate of Mn binding should decrease. Examination of the shapes of the  $R_{pc}$  curves for Mn oxidation indicate that the first order approximation is not entirely warranted. In T80-18.0, the maximum Mn removal rate occurs at the sediment-water interface, and large changes in solid and solution Mn concentrations in this region result in poor resolution, limiting the value of this treatment. The  $R_{pc}$  profiles for T80-13.0 and T80-8.0 are also not in agreement with first order kinetics. It is impossible to prove that the Mn oxidation rates are first order with respect to  $\text{Mn}^{2+}$  concentration and if microbial participation in this process is occurring.

#### Iron Oxidation

The oxidation of Fe in natural waters follows the rate law (Stumm and Morgan, 1981; Davison and Seed, 1983):

$$(20) \quad -d [\text{Fe}^{2+}]/dt = K_{ox} * [\text{Fe}^{2+}] * p\text{O}_2 * [\text{OH}]^2$$

where  $[\text{Fe}^{2+}]$  and  $[\text{OH}^-]$  are molar activities,  $p\text{O}_2$  is the partial pressure of oxygen, and  $K_{ox}$  is approximately  $2 * 10^{13} \text{ (mol L}^{-1}\text{)}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  (Davison and Seed, 1983). Using the  $R_{pc}$  values calculated from the Fe model, maximum Fe oxidation rates of 3.5 to 12.7  $\text{umol Fe}^{2+} \text{ cm}^{-3} \text{ yr}^{-1}$  or  $1.9 * 10^{-9}$  to  $6.9 * 10^{-9} \text{ mol L}^{-1} \text{ min}^{-1}$  may be calculated.

Substituting these into equation 20 with appropriate concentrations of  $\text{Fe}^{2+}$  and  $\text{OH}^-$ ,  $\text{pO}_2$  values of 0.035 to 0.085 atm may be calculated. These values seem fairly high, and correspond to pE's of 13.2 to 13.6. Since Mn reduction is occurring in the zone of Fe oxidation, a more realistic pE for the Fe oxidizing zone is probably 10 or less. It is obvious that Fe oxidation is occurring more rapidly than equation 20 would predict, perhaps because this oxidation may be coupled to Mn reduction.

Sung and Morgan (1980) have shown that for pH's  $\geq 7.0$  the oxidation of  $\text{Fe}^{2+}$  has an autocatalytic component. Davison and Seed (1983) have shown that the addition of  $50 \text{ mg L}^{-1}$  of Fe(III) gel increases the Fe oxidation rate two to five times. In Toolik sediment, Fe oxidation occurs in a sediment environment which can have over  $15000 \text{ mg L}^{-1}$  Fe(III) and similar concentrations of Mn(IV). The simple rate expression in equation 20 should probably be replaced by an autocatalytic one such as for  $\text{Mn}^{2+}$  oxidation. As in the case of  $\text{Mn}^{2+}$  oxidation, the role of microbes in oxidizing  $\text{Fe}^{2+}$  in these sediments is unknown. Fenchel and Blackburn (1979) cite numerous studies in which microbial oxidation of  $\text{Fe}^{2+}$  occurs. Simple one point estimations of first order rate constants for  $\text{Fe}^{2+}$  oxidation are on the order of  $100 \text{ to } 300 \text{ yr}^{-1}$ , somewhat higher than indicated for Mn oxidation. This result is consistent with the observation that Fe oxidation occurs in a more restricted zone than does Mn oxidation.

### CONTROL OF PORE WATER CHEMISTRY: CONCLUSIONS

On the basis of the solubility calculations and diagenetic modelling presented in this chapter, several conclusions can be made about the processes which regulate the concentrations of Mn, Fe and P in interstitial solution.

Inorganic phosphorus in pore water is controlled by two processes, one occurring above the vivianite saturation zone and the other within it. Above this zone, inorganic P is associated with Fe(III) oxyhydroxides and a distinct P enrichment is found. A mechanism involving the dissolution, diffusion and precipitation of inorganic P concentrates P in oxidized zones within lacustrine sediments (Carignan and Flett 1981) and is the probable mechanism for regulating P concentration in the upper part of profundal sediments. Below the saturation zone, the concentration of pore water  $\text{PO}_4$  is regulated by formation of authigenic phosphate minerals. Thus, in the upper parts of these cores, pore water  $\text{PO}_4$  concentrations are regulated by adsorption and upward diffusion of  $\text{PO}_4$  towards oxidized horizons. Deeper within cores the precipitation of  $\text{PO}_4$  as Mn(II) and Fe(II) minerals regulates pore water concentrations.

Diagenetic modelling has indicated that reduction of Mn and Fe oxides can account for the observed pore water Mn and Fe distributions. Several cores have lower  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  concentrations at greater depths within the core, suggesting that at least in some cores, Mn and Fe are being removed from pore water in forms other than oxides. Precipitation as reduced phosphates is occurring for both Mn

and Fe, but high  $\text{Fe}^{2+}:\text{PO}_4$  and  $\text{Mn}^{2+}:\text{PO}_4$  ratios suggest that removal as phosphates is not a quantitatively important process. Absence of detailed knowledge of the amounts of mixed Fe(II)-Mn(II) phosphates precludes the use of mass balances to assess the importance of this metal removal mechanism.

The major results of this study may be summarized:

1. Near the sediment-water interface, the rates of diffusion of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  and the rates of the reduction/oxidation reactions are the principal controls of Fe and Mn pore water concentrations.
2. The formation of authigenic vivianite and Fe(III)-phosphate complexes (adsorption) are important in the regulation of pore water phosphate concentrations.
3. First order models of metal oxidation and reduction fit some pore water solid phase and pore water data quite well, but the mechanisms which control these reactions were not determined.
4. Manganese reduction may be coupled to Fe oxidation in these sediments, but more data is necessary before the existence of this process is proven.



## CHAPTER 6. TRACE ELEMENT DIAGENESIS AND DISTRIBUTION

The association of trace elements with hydrous Mn and Fe oxides is an important mechanism for limiting the solubility of trace elements in natural waters (Jenne, 1968; Lee, 1975; Murray, 1975; Gadde and Laitinen, 1974). Selective leaching of different sediment fractions has indicated that these oxides are important sites for the retention of trace elements in suspended particulates and in sediments (Calvert and Price, 1977; Sozanski and Cronan, 1979; Gibbs, 1977).

In Toolik Lake sediment, extremely high concentrations of Mn and Fe oxides result from post-depositional migration within sediments, and the different solubilities of Mn and Fe oxides result in the separation of Mn and Fe into distinct crusts. Local anthropogenic influences on trace metal loading in Toolik Lake is restricted to the early 1970's, limiting the impact of watershed disturbance to the top-most section of most cores. The purpose of this chapter is to investigate the following hypothesis: Mn and Fe diagenesis in lacustrine sediments has a significant impact upon the distribution of trace elements.

Toolik Lake should be an excellent site for the examination of this hypothesis because of high concentrations of sediment Mn and Fe, large  $Mn^{2+}$  and  $Fe^{2+}$  fluxes within sediments, low anthropogenic inputs of trace elements, low rates of bioturbation and the chemical separation of Mn and Fe. The scope of this chapter is limited to the investigation of diagenetic trace element remobilization. Extensive

discussion of trace element loading rates and the concentration of trace elements in surficial sediment will not be presented here.

## METHODS

The samples used in this study are from four Pb-210 cores presented in Chapter 4. Dried, ground sediment samples were digested in  $\text{HNO}_3$ -HCl using the technique of Evans and Rigler(1980), in which 0.25 g of dried sediment was digested in 2 ml  $\text{HNO}_3$  and 4 ml HCl at  $70^\circ\text{C}$  until dryness. Ten ml of 1.5 N HCl was added to the sediment, the mixture was briefly heated, and the solution removed by pipet after allowing the sediment to settle. A Perkin-Elmer 603 atomic absorption spectrophotometer was used for analysis of Cu, Ni, Zn, Cr, Co and Ba. Blanks were carried through the entire procedure. Lead was not analyzed because of its extremely low concentrations ( $<10$  ug/g). Molybdenum was analyzed by graphite tube atomic absorption spectroscopy.

Carbonate C was analyzed using the procedure of Stainton (1973) and organic C was calculated as the difference between carbonate C and total C as determined on a Hewlett-Packard 240-C CHN analyzer. Total digestions for major elements were done by  $\text{LiBO}_2$  fusion, as described in previous chapters.

Radium-226 was determined via the radon emanation method on 6.0 N HCl digests by D. Glover. Graphite tube atomic absorption spectrophotometry was used to determine the interstitial  $\text{Ba}^{2+}$  concentration on a separate core.

Duplicate analyses of 11 samples show coefficients of variation of less than 10% for all trace metals. Counting statistics indicate that the Ra-226 analyses are good to approximately 10% (D. Glover, personal communication). The coefficients of variation of total C and carbonate C are less than 5% and 10% respectively.

## RESULTS

Figures 6-1, 6-2, 6-3 and 6-4 show the major and trace element data for cores T80-18.0, T80-8.0, T79C-6.0 and T80-5.5. All of the data have been normalized to the Al concentration, yielding concentrations in ug per g total Al. This normalization removes the influence of sediment dilution by metal oxides (Chapters 3 and 4). The original data are presented in Appendix E.

The concentrations of trace and major metals in Toolik Lake sediments are quite similar to those found in "oxidate crusts" in Lake Windermere (Gorham and Swaine, 1965) and in ferromanganese concretions from Shebandowan Lakes, Ontario (Sozanski and Cronan, 1979). The range of values on a total sediment basis is presented in Figure 6-5, the Toolik values coming from the four cores for which trace metal values were determined. The range shown in Figure 6-5 is the same as that found for 12 surficial sediment samples.

The shaded areas in the sediment profiles represent the concentration of each element above an assumed "background" value, usually determined from constant element to Al ratios deep in these cores. Manganese, Fe, Ba, carbonate C, Ca, Co, Mo and P have the greatest

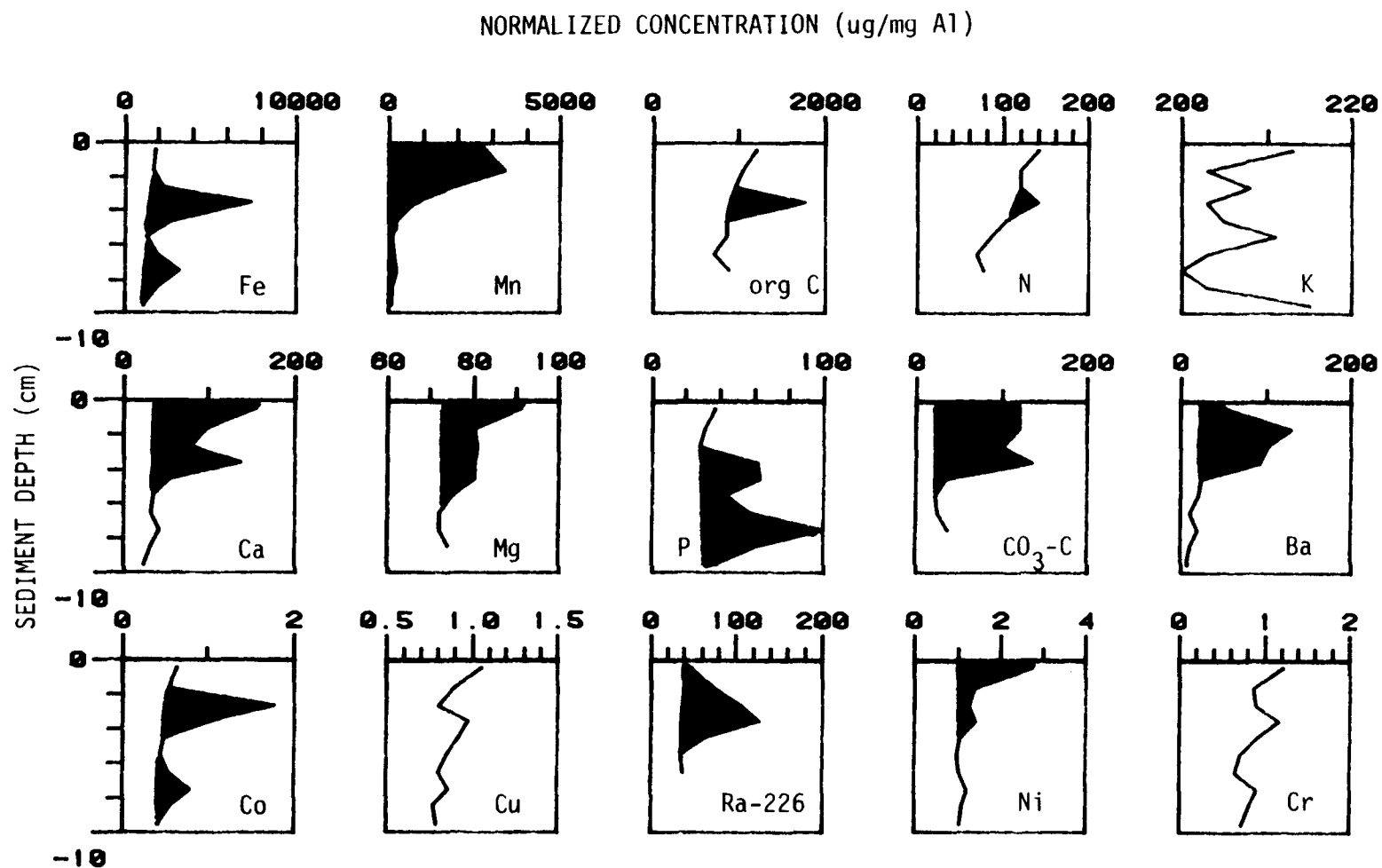


Figure 6-1. Major and trace metal data for core T80-18.0. Data have been normalized to the Al concentration. The shading represents concentrations of each element above background values.

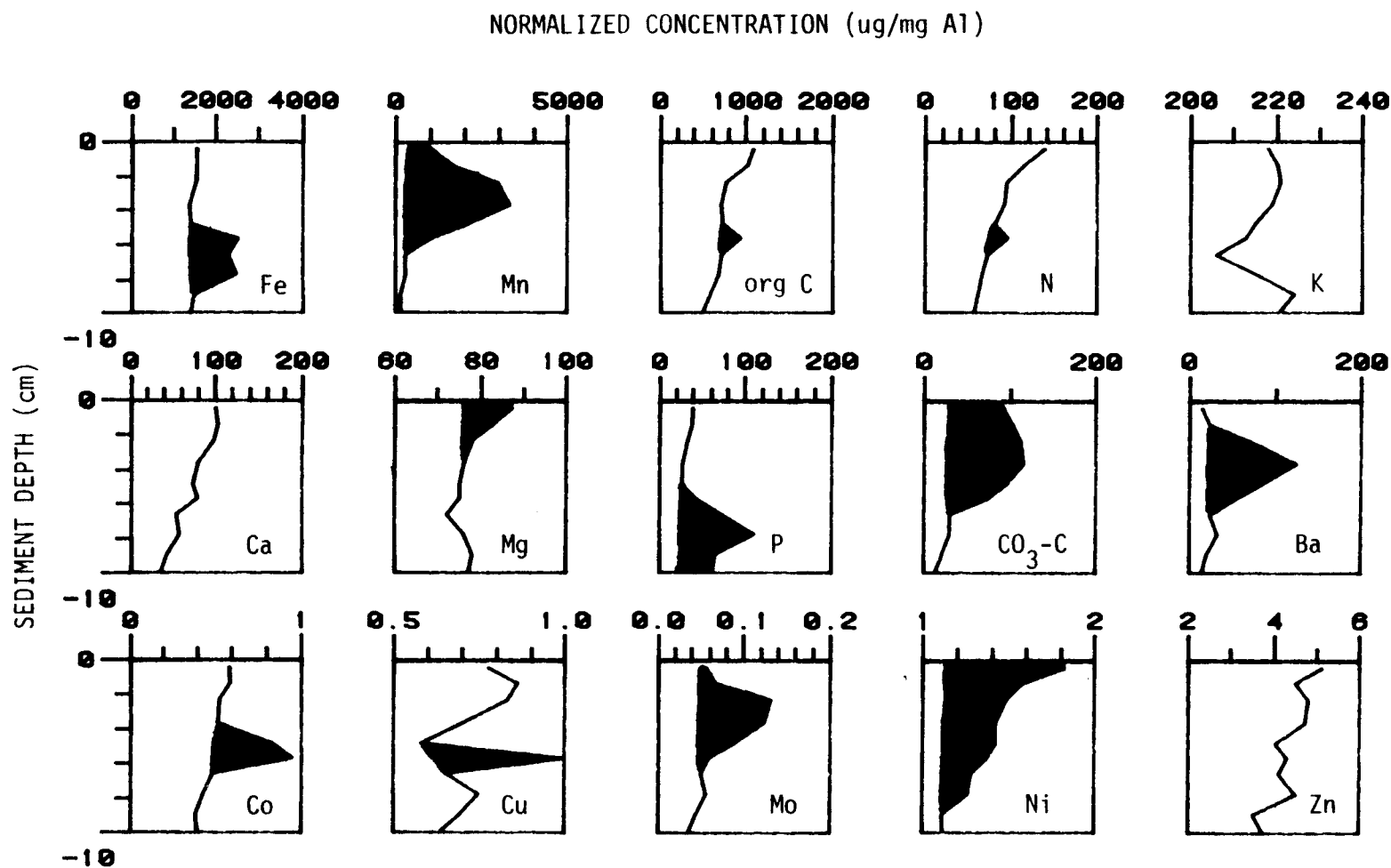


Figure 6-2. Major and trace element data for core T80-8.0. Data have been normalized to the Al concentration. The shading represents concentrations of each element above background values.

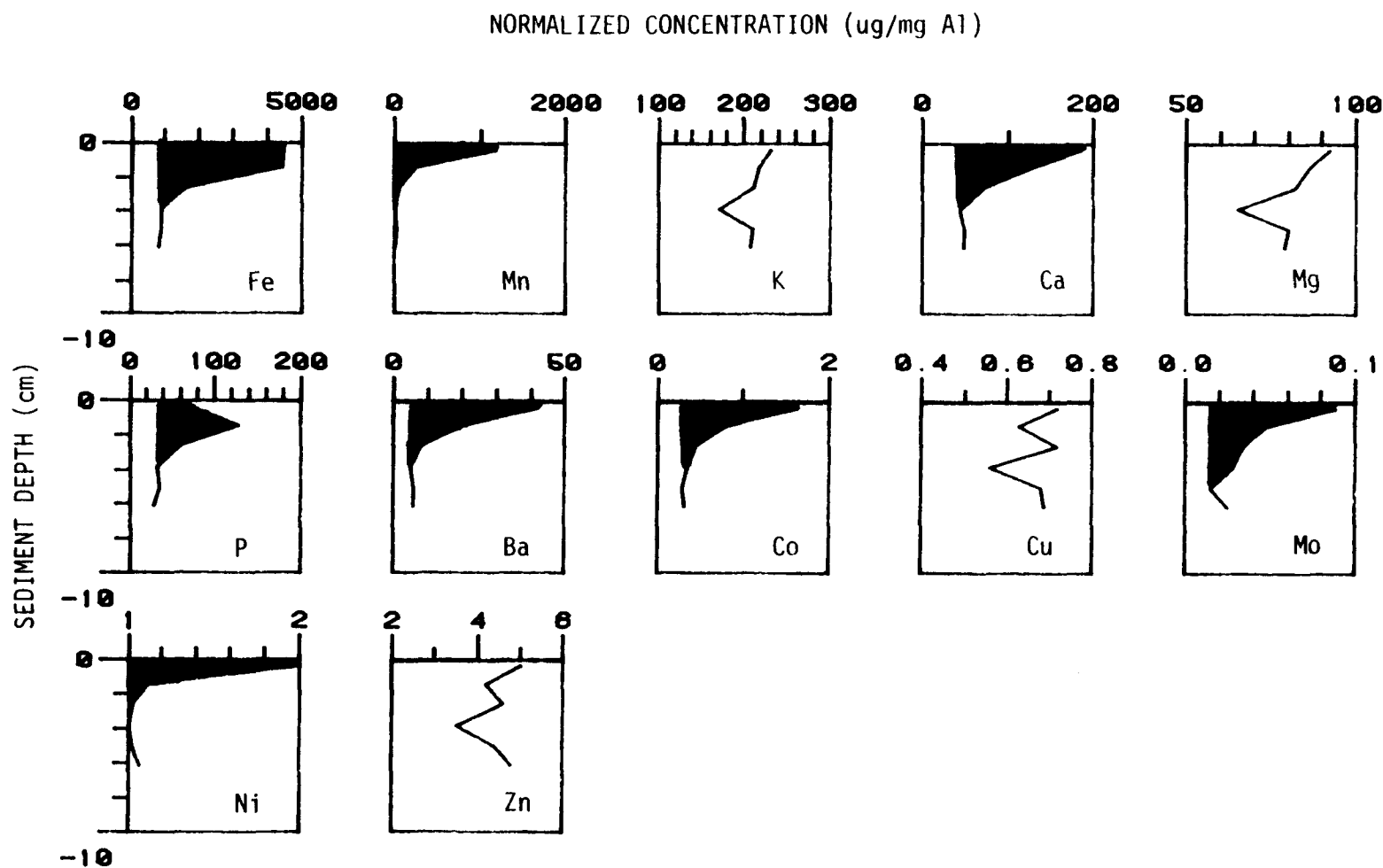


Figure 6-3. Major and trace element data for core T79C-6.0. Data have been normalized to the Al concentration. The shading represents concentrations of each element above background values.

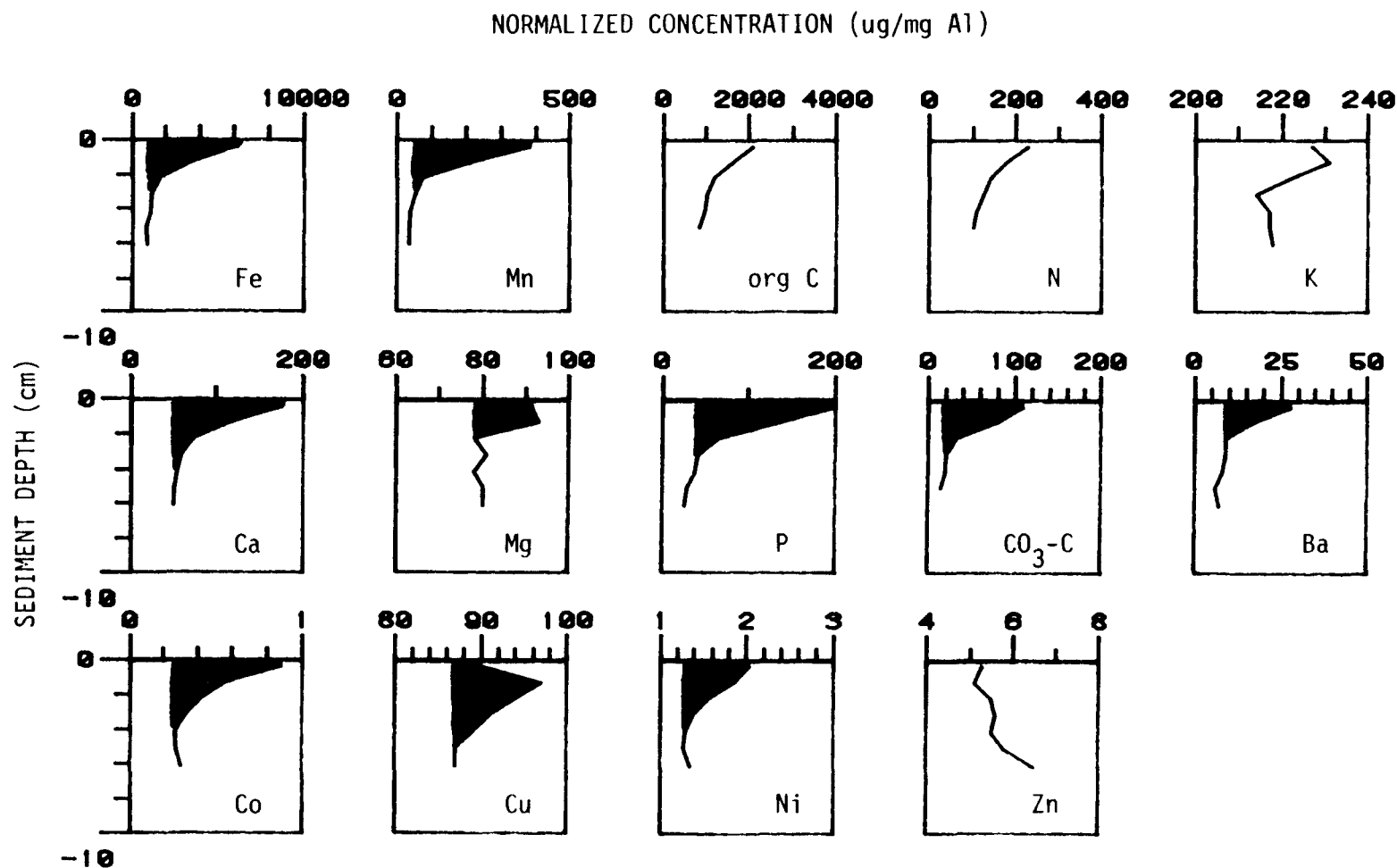


Figure 6-4. Major and trace element data for core T80-5.5. Data have been normalized to the Al concentration. The shading represents concentrations of each element above background values.

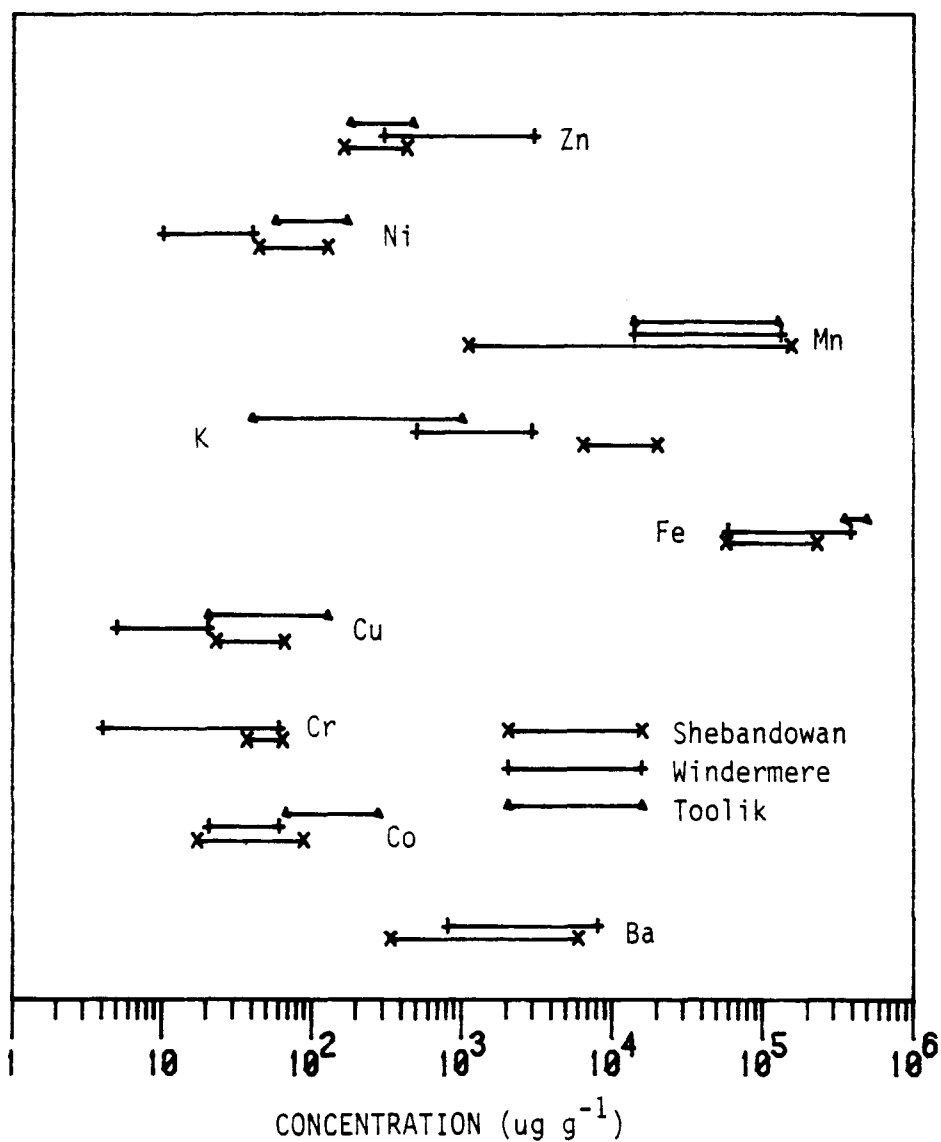


Figure 6-5. The range of concentration of major and minor metals in Toolik Lake cores, ferromanganese concretions from the Shebandowan Lakes (Sozanski and Cronan, 1979) and oxidate crusts in Lake Windermere (Gorham and Swaine, 1965).



variability in these cores, the highest values being over twice the background concentration. Magnesium, organic C, Ni and Cu have intermediate amounts of variability, and K and Zn have no well established trends in concentration variation.

The four cores presented here have important differences in their major metal distributions. T80-18.0 and T80-8.0 have well developed Mn crusts, and T80-18.0 has a thin Fe crust. T79C-6.0 and T80-5.5 have maximum concentrations of Mn and Fe at the sediment-water interface, and the distribution of Mn and Fe is quite similar in both cores. T79C-6.0 has the highest sedimentation rate of any core in this study.

In Mn- and Fe-rich sediment zones, there are greatly elevated concentrations of Ba, Ca, carbonate C, Ni and Ra-226, smaller changes in Cu and Mg, and negligible changes in Zn and K. Barium and carbonate C profiles are very similar to Mn profiles in all cores. In T80-5.5 and T79C-6.0, Co, Ca, Ni and Mg all show concentration maxima at the sediment-water interface. In T80-8.0 and T80-18.0, Ni, Mg and Ca have maximum concentrations at the sediment-water interface and Co has its maximum at or just above the top of the Fe-rich zone, near the bottom of the Mn crust. The profile of Ra-226 in T80-18.0 is very similar to that of Co. The organic C:N ratios in Fe-rich zones in T80-8.0 and T80-18.0 are quite high and the concentration of organic C is higher than in adjacent sediment horizons.

## DISCUSSION

These data support the hypothesis that the diagenesis of Mn and Fe affects the distribution of trace elements in lacustrine sediments. The geochemistry of carbonate, Ca, Co, Ra-226, Ba and Ni are dominated by diagenetic redistribution processes, with other sediment components also showing effects. The reduction/diffusion/oxidation process which redistributes Mn and Fe is probably the principal mechanism concentrating minor elements in the more oxidized sediment horizons.

The concentrations of trace metals found in Toolik Lake sediments and associated crusts (Figure 6-5) are similar to those in other unpolluted lake sediments and lacustrine ferromanganese concretions (Forstner and Wittmann, 1979; Sozanski and Cronan, 1979; Gorham and Swaine, 1965; Calvert and Price, 1977). The chief differences between this study and others are that the Mn- and Fe-rich crusts occur as steady state features of accumulating sediment and the association of trace elements with metal oxides must result from redistribution within the sediment. There is no apparent need to invoke water column processes to explain the occurrence of metal rich zones.

The harsh extraction procedure used in this study may mask associations between some trace elements and metal oxides, especially in the cases where only a small portion of the total acid extractable metal is retained by oxides. Processes such as metal retention by organic matter, clay minerals or within crystal lattices cannot be directly separated from adsorption or coprecipitation with Mn and Fe oxides.

The actual mechanisms of incorporation of trace elements into the Fe- and Mn-rich zones cannot be determined from solid phase extraction of metals. Some  $\text{Ba}^{2+}$  in solution may coprecipitate with  $\text{Mn}^{2+}$  to form psilomelane ( $\text{BaMn}_8\text{O}_{16}(\text{OH})_4$ ; Calvert and Price, 1977). If all Ba was present as psilomelane, between 1.6 and 29% of sediment Mn could be present in this mineral. The relationship between interstitial  $\text{Ba}^{2+}$  and solid phase Ba is very similar to that observed for  $\text{Mn}^{2+}$  and solid phase Mn throughout this study (Figure 6-6). Apparently, a similar dissolution/diffusion/precipitation mechanism can account for Ba enrichments within Mn-rich sediment horizons. The Ba:Mn ratios in the solid phase increase with depth throughout cores T80-18.0, T80-8.0 and T79C-6.0, suggesting that  $\text{Ba}^{2+}$  does not diffuse as far as  $\text{Mn}^{2+}$  within the zone where  $\text{Mn}^{2+}$  is oxidized, and that the solubilities of Ba-Mn minerals or adsorbed complexes are lower than other Mn oxides.

Mechanisms have been proposed to account for the association of trace elements with Mn and Fe oxides. These include the incorporation of transition elements in Mn oxide structures (Giovanolli *et al.*, 1975), electrostatic and specific adsorption processes (Jenne, 1968; Gadde and Laitinen, 1974; Murray, 1975; Stumm and Morgan, 1981), electron exchange on the surface of Mn(II)-Mn(IV) oxides (Hem, 1978; 1980) and the adsorption of metal ligand complexes or adsorption of uncomplexed metals to oxide-humic complexes (Davis and Leckie, 1978). The presence of relatively high concentrations of organic material in Toolik Lake sediment may have a significant effect on the chemistry of metals. The low organic C/N ratios in Fe enriched zones in T80-18.0

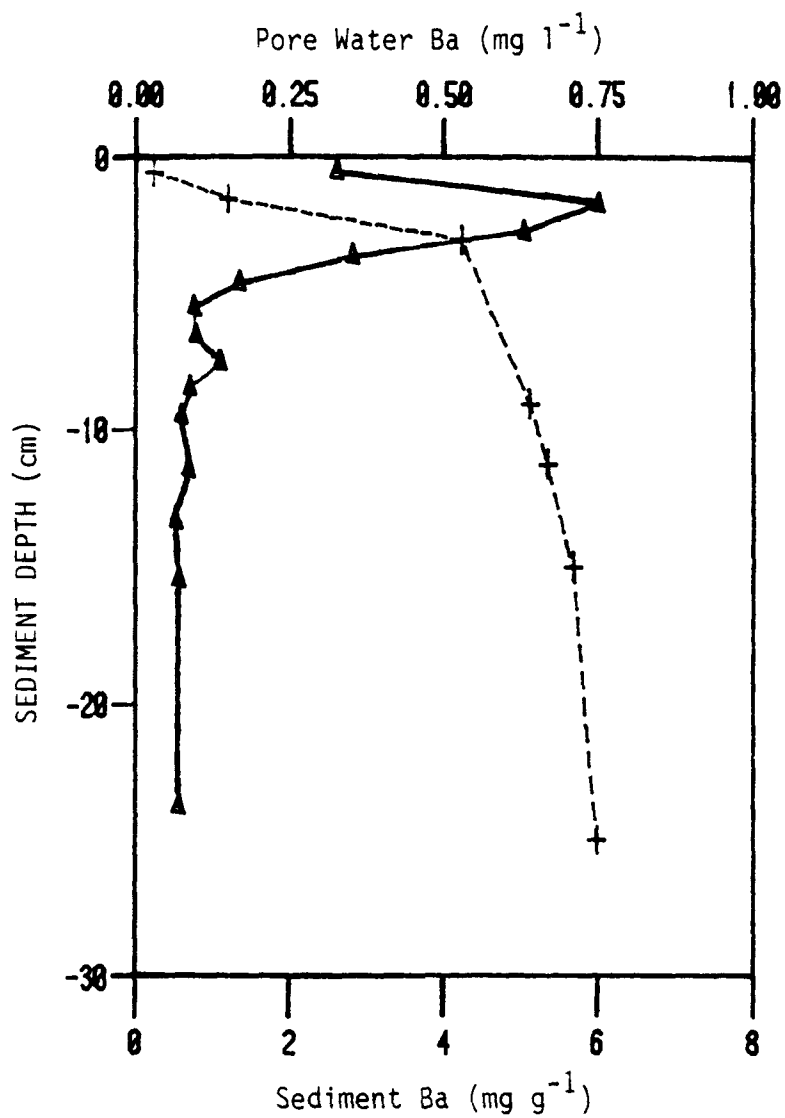


Figure 6-6. Interstitial Ba<sup>2+</sup> and sediment Ba concentrations in cores from the 18.0 m. location. The solid phase and pore water data are from different cores.

and T80-8.0 and the concurrent high organic matter content suggest that the Fe is adsorbing low N organic materials. Tipping (1981) has shown that sorption of humic matter onto iron oxides occurs in natural systems, and maximum humic adsorption on Fe gels at pH 7.2 ranged from 146 to 224 mg humic per g Fe oxide, depending on the age of the oxide. Estimates of the humic concentrations in the Fe rich horizons in T80-18.0 and T80-8.0 range from approximately 70 to 180 mg humic per g  $\text{Fe}(\text{OH})_3$ , below the maximum amounts estimated by Tipping. Metals such as Cu, which are strongly bound by organic matter, may become associated with oxides via organic intermediaries.

Elevated carbonate C concentrations cannot be explained using saturation calculations, because pore waters in the oxidized zone are undersaturated with respect to  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{MnCO}_3$  and  $\text{FeCO}_3$ . Detrital Ca and Mg carbonates cannot account for more than 40% of this enrichment, so it seems likely that the carbonate C is associated with Mn and perhaps Fe. Calvert and Price describe mixed Mn-Fe-Ca carbonates in some lacustrine ferromanganese nodules, but solution data has not been presented for solubility calculations.

The results of this work have implications for the study of metal accumulation rates in sediments from polluted systems. Recent studies have interpreted increased concentrations of transition metals in surficial sediments as evidence for elevated rates of metal flux to sediment resulting from anthropogenic inputs (Bruland *et al.*, 1974; Edgington and Robbins, 1976; and many others). Although it seems certain that the predominant cause of increased concentrations of metals

in these studies is pollution, it should be recognized that in oxidized sediments with moderate to high concentrations of Mn and Fe oxides, the potential exists for improperly assigning the cause of elevated metal concentrations. Profiles of Ba, Ni and Co in T80-5.5 and T79C-6.0 could easily be misinterpreted in this manner. Similarly, Carignan and Flett (1981) have shown that the profiles of P in lacustrine sediments must be examined for diagenetic redistribution before the interpretation of anthropogenic influences can be made. In reducing sediments with low Mn and Fe oxide concentrations, fixation of transition metals as sulfides should decrease the diagenetic remobilization of these metals.

Few other studies have examined the distribution of trace elements in accumulating sediments with high Mn and Fe concentrations. Large post-depositional migrations of Mn occur in marine sediments (Trefry and Presley, 1982; Froelich et al., 1979) and in freshwater sediments (Robbins and Callender, 1975; Tessenow and Baynes, 1975), but the effects of Mn diagenesis upon trace metal distribution have not been examined in detail. Tsunogai et al. (1979) proposed that Cu, Zn, Co and Pb migrate with Mn in pelagic marine sediments, and form horizons somewhat enriched in these transition elements. The results from Toolik Lake sediment show the effects of redox driven Mn and Fe redistribution upon the geochemistry of trace elements better than any other study. The exceedingly high concentrations of Mn and Fe in both solution and solid phases, the low sedimentation rates and the successful coupling of solid and dissolved phases in a diagenetic

model make metal oxide and trace metal distributions better understood in this system than is usually possible in other systems.

## CHAPTER 7.      MASS BALANCES AND CONCLUSIONS

This final chapter has four main purposes: to synthesize and integrate the various measurements of pool sizes and flux rates of elements in Toolik Lake into a macroscopic view of Mn, Fe and P cycling; to review the processes which result in Mn and Fe rich crusts and nodules in lakes; to summarize the major findings of this research; and to suggest new research areas pertinent to this work. The data for Mn, Fe and P budget calculations have been presented in the previous chapters.

Toolik Lake mass balances for Fe, Mn and P are the most detailed prepared for any arctic lake, and for Mn and Fe represent one of the first budgets available for oligotrophic lakes. The terms in the mass balances come from four different sources: 1. watershed and lake mass balances; 2. sediment traps; 3. Pb-210 sedimentation rates and; 4. modelling of sediment diagenesis. This budget includes only the 1980 stream data.



## MANGANESE AND IRON GEOCHEMISTRY IN TOOLIK LAKE

### Manganese and Iron Budgets

The budgets for Mn and Fe (Figures 7-1, 7-2) combine several independent measures of lake retention of metals. The calculation of the sediment budget will be described; the water column budget calculations can be found in Chapter 2.

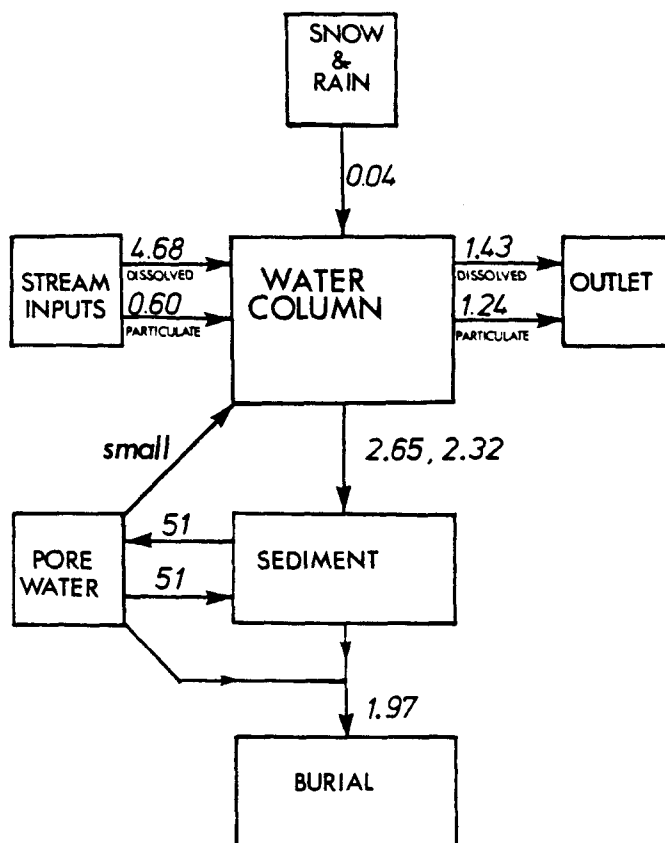
The Mn and Fe budget terms for burial below the metal enriched zones utilize the Pb-210 sedimentation rates and solid phase concentrations of Mn and Fe. The calculation of Fe burial rate has been adjusted because the relatively mild water column TFe methods recover only  $54 \pm 13\%$  of the total Fe in the sediment. The burial rates of Mn and Fe were obtained for each core (Table 7-1) and a lake-wide rate was estimated using the fraction of lake bottom in a number of depth intervals (0-2.5, 2.5-5.0, 5.0-10.0, 10.0-15.0 and 15.0-25.0 m).

The diagenetic flux rates are estimates based on modelled rates of dissolution of Mn and Fe oxides in 12 cores. I have assumed that oxidation equals reduction within sediments, realizing that some oxidation may occur within the water column. On a lake-wide basis, fluxes of dissolved metals out of sediments are probably balanced by their rapid oxidation and sedimentation.

The important features of these Mn and Fe budgets and the overall cycle are:

1. Precipitation inputs of metals to the lake are small.
2. Solute inputs from streams are higher than particulate inputs (if

# MANGANESE



$\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$

Figure 7-1. Manganese cycle for Toolik Lake. All fluxes are normalized to the area of the lake. Two rates of Mn flux from the water column to sediment are included, the first ( $2.65 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) coming from the 1980 stream budget and the second ( $2.32 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) from the sediment traps in 1981. The sediment Mn burial rate is from Pb-210 derived sedimentation rates.

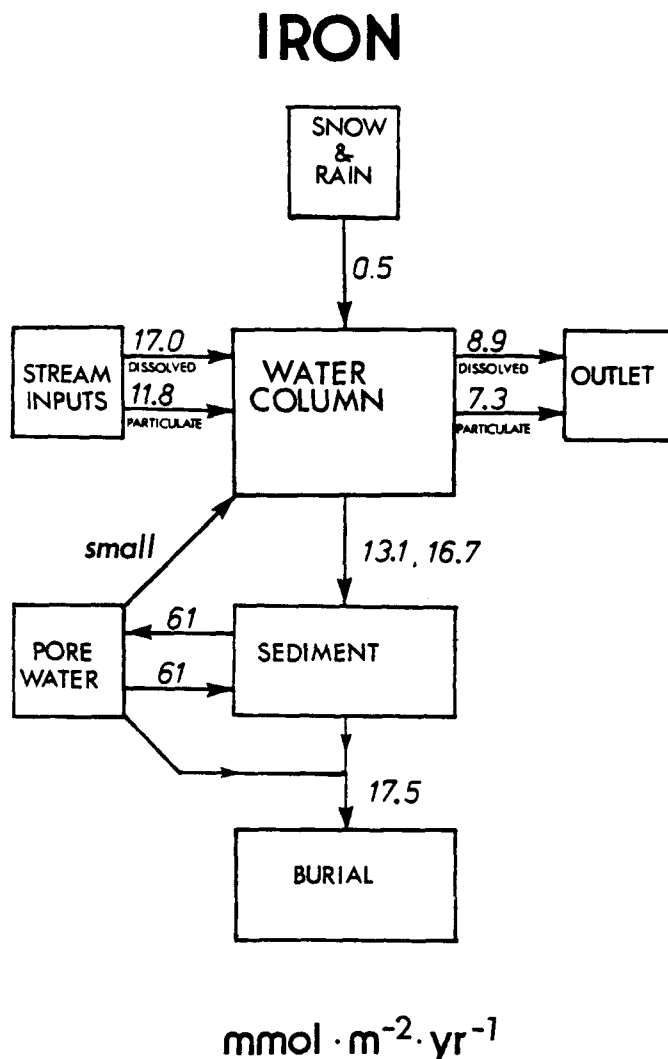


Figure 7-2. Iron cycle for Toolik Lake. All fluxes are normalized to the area of the lake. Two rates of Fe flux from the water column to sediment are included, the first ( $13.1 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) coming from the 1980 stream budget and the second ( $16.7 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) coming from the sediment traps. The acid reducible sediment Fe burial rate ( $17.5 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) is from Pb-210 derived sedimentation rates and is 54% of the total Fe rate.

Table 7-1. Manganese and iron sedimentation; oxide crusts and permanent burial.

Location	Mn Flux <sup>a</sup> (mmol m <sup>-2</sup> yr <sup>-1</sup> )	Excess Mn <sup>b</sup> (mmol m <sup>-2</sup> )	Time <sup>c</sup> (yr)	Fe Flux <sup>a</sup> (mmol m <sup>-2</sup> yr <sup>-1</sup> )	Excess Fe <sup>b</sup> (mmol m <sup>-2</sup> )	Time <sup>c</sup> (yr)
T80- 3.5	0.08	43	540	4.2	2500	600
T80- 5.5	0.80	630	790	17.6	9000	510
T80- 8.0	5.04	10200	2020	44.7	4000	90
T80- 11.0	2.26	8980	3970	40.0	12000	300
T80- 13.0	2.88	14100	4900	64.7	5000	80
T80- 18.0	3.75	6680	1780	76.3	4000	50
T79A- 5.5	0.17	9	50	19.2	250	13
T79C- 6.0	1.50	940	630	66.2	7000	110
T79D-10.0	0.23	10	40	22.3	1000	45
T79E- 7.5	5.00	4490	900	53.4	12000	220
T79F- 7.0	7.00	3570	510	111.5	10000	90
T79G- 6.0	0.57	25	40	49.0	1000	20
CB80- 8.0	0.29	44	150	31.7	2000	60
water column	2.65	-	-	13.1	-	-
sediment traps	2.32	-	-	16.7	-	-
sediment accumulation	1.97 <sup>d</sup>	3350 <sup>d</sup>	-	17.5 <sup>d</sup>	3540 <sup>d</sup>	-
mean of above	2.31 ± 0.34	3350	1450	15.8 ± 2.3	3540	225

a. This is the burial rate of Mn and Fe below the enriched zones.

b. Diagenetic oxides.

c. Time it would take to accumulate excess metal at the present burial rate.

d. On a lakewide basis, using the hypsographic curve.

the unmeasured PFe is not included).

3. The water column cycle of Mn is dominated by large inputs (over 70% of yearly DMn) in early spring flow.

4. Approximately 70% of incoming DMn is converted to PMn in the lake, and almost 50% of DFe is retained. Overall, 50% of TMn and 55% of TFe are retained.

5. Daily water column removal rates for Mn and Fe (from sediment traps) have the same seasonal trend as rates of primary productivity and nutrient sedimentation. A biological mechanism for water column removal of metals is implied.

6. Rates of Mn and Fe sedimentation calculated by three techniques (stream mass balance, sediment traps and Pb-210 sedimentation) yield similar rates. This is the first successful test of the Pb-210 sediment accumulation rate technique for metal retention estimates. This shows the utility of Pb-210 rates for estimating rates of metal accumulation in a system for which independent estimates are available.

7. The rates of sediment reduction and oxidation are much larger than any other terms in these budgets. If oxidized surface sediments were not retaining these metals, the water column would have very large fluxes of dissolved metals from sediments.

8. The labile nature of Mn and Fe in Toolik Lake sediments arises from their endogenic origin; much of the Mn and Fe retained in the lake enters it in dissolved form.

### Manganese and Iron Rich Sediments: Putting Toolik Lake in Perspective

Ferromanganese concretions have been found in lakes from many parts of the world (Calvert and Price, 1977). The formation of concretions, both crusts within the sediment and nodules on the sediment surface, is dependent upon the flux of diagenetically mobile Mn and Fe to the sediment surface and upon processes which redistribute these elements within sediment. The watershed influx of Fe and Mn to lakes is enhanced by wet, cool soils with high organic content (Calvert and Price, 1977), conditions commonly found in formerly glaciated regions in which soils have changed from basic to acidic environments and in which unconsolidated rock is found (Strakhov, 1966). The Toolik Lake area consists of glacial outwash, the tundra has low pH and abundant organic matter and the soil is enriched in Mn and Fe. These factors, combined with a low input of terrestrial inorganic material which would dilute the sediment Mn and Fe, make Toolik Lake a likely environment for oxide crust formation.

Diagenetic remobilization of Mn and Fe is important in the formation of lacustrine concretions (Calvert and Price, 1977; Sozanski and Cronan, 1979; Dean et al., 1981); the general mechanism cited is a reduction/transport/oxidation process. The chief differences in the cycles of Mn and Fe in different lakes are related to the locations where each of these processes occur. Rapid mixing processes in the water column of eutrophic Oneida Lake keep the water column oxic, and Dean et al. (1981) have shown that  $Mn^{2+}$  is released to the water column from reducing profundal sediments. The  $Mn^{2+}$  is mixed

throughout the water column and is oxidized to Mn(IV) oxides via the mediation of algae and bacteria. On hard substrate with negligible sediment accumulation, Mn rich nodules are forming at the well oxygenated sediment-water interface. Transport of these nodules downslope to reducing sediments occurs via physical processes, and the cycle continues. Concretions at the surface of Shebandowan Lake sediment (Sozanski and Cronan, 1979) result from upward and lateral transport of  $\text{Mn}^{2+}$  from reducing sediments, and as in the case of Oneida Lake, the sediment underlying most of the concretions was quite coarse.

Strakhov (1966) outlined a similar mechanism for forming Mn-Fe concretions. In very oligotrophic lakes, Mn and Fe crusts are formed by upward diffusion of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  to the oxic sediment-water interface. Bottom water dissolved oxygen decreases in more productive lakes and there is a tendency for Mn and sometimes Fe to accumulate at lesser water depths, where oxygen is still present. Manganese and Fe are not present as concretions in very eutrophic lakes, except in oxidized, high energy systems such as Oneida Lake.

Toolik Lake sediment represents a very oligotrophic end member of Strakhov's scheme. Low rates of organic matter oxidation in profundal sediment lead to Mn and Fe enrichments in the upper 5 to 10 cm of sediment and a vertical separation of Mn and Fe. Reducing conditions in littoral sediments, a result of more organic carbon oxidation, causes Mn(IV) reduction and a loss of  $\text{Mn}^{2+}$  to the water column, where it is mixed throughout the lake. This process eventually incorporates

Mn into profundal sediments where it is retained. This process does not concentrate Fe in profundal sediment (from littoral sediment) because Fe has a much lower solubility and faster oxidation rates (Stumm and Morgan, 1981) which allow very little  $\text{Fe}^{2+}$  to diffuse into the water column. Greater inputs of electron acceptors such as Mn(IV) help to create a more oxidizing environment and organic carbon input alone is not the sole factor responsible for the observed solid phase Mn distribution.

A key factor in the formation of discrete nodules and concretions, as opposed to crusts within sediments, is the nature of the substrate. In eutrophic lakes, a negligible accumulation rate of sediment is necessary to maintain metal oxides within oxygen bearing water. Oligotrophic lakes such as Toolik Lake have more weakly reducing conditions in the soft profundal muds, leading to the formation of metal crusts within the sediment.

#### Metal Cycling and its Role in Organic Matter Oxidation

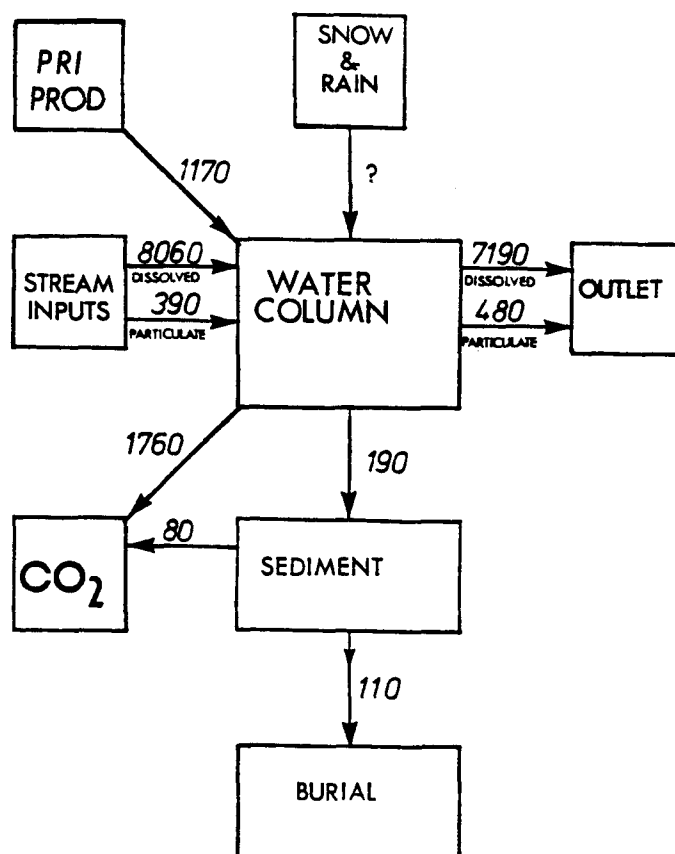
The quantitative significance of the reduction of Mn(IV) and Fe(III) to the oxidation of organic matter has been examined in few other studies. In eutrophic Lake Vechten, accumulation of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  in the anoxic hypolimnion represents reducing equivalents equal to 1% of primary production (Verdouw and Dekkers, 1980). The reduction of Mn(IV) and Fe(II) averaged 3.3% of anoxic C metabolism (this excludes dissolved oxygen as an electron acceptor) in three Canadian Shield lakes (Kelley et al., 1982). Sulfate reduction plus



methanogenesis accounted for 91 to 98% of C metabolism. In deep sea sediments, metal reduction represents large capacities for organic matter oxidation, but the role of Mn and Fe in sediment redox processes is poorly understood and may consist mainly of the cycling of other reduced compounds (Reeburgh, 1983).

In Toolik Lake, the rate of sediment cycling of carbon (other than processes occurring in the top few millimeters of sediment) is not quantitatively important (Figure 7-3). The oxic mineralization of C within the water column and surficial sediment is over 20 times the rate of mineralization within the sediment. The reduction of Mn and Fe yields reducing equivalents up to half of total sediment C mineralization, but this amount would be lowered to approximately 10% if Mn reduction occurred only as a result of Fe(II) oxidation. The rate of sediment accumulation of organic C in Figure 7-3 is an underestimate of the true rate of C sedimentation, because the top 1.0 cm of sediment consists of sediment from 0 to 10 yr old, and substantial rates of C mineralization may occur in the oxygen rich first few millimeters of sediment. Because sulfate reduction and methanogenesis are probably unimportant in Toolik Lake, the reduction of metals constitutes the most important mechanism in anoxic C metabolism. In eutrophic Canadian Shield lakes and in Lake Vechten, the reduction of Mn and Fe plays a less important role.

## ORGANIC CARBON



$\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$

Figure 7-3. Carbon cycle for Toolik Lake. All fluxes are normalized to the area of the lake. The C flux from the water column ( $190 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) has been derived from Pb-210 sedimentation rates and the surficial sediment (0-1 cm) organic C content, and should be regarded as an underestimate of this flux. Fluxes to the  $\text{CO}_2$  pool are calculated by difference.

### Evolution of Manganese and Iron Crusts

The final aspect of metal cycling that will be considered is speculation upon the evolution of metal oxide crusts in the bottom of Toolik Lake. A question to be addressed is: In 12,000 years, when the lake is twice as old as now, will the Mn and Fe rich crusts have more Mn and Fe than they do now? Table 7-1 presents the data pertaining to this question. The excess Mn and Fe values described in Chapter 5 are presented, as well as the sedimentation rate of Mn and Fe below the region of excess Mn and Fe. The general agreement between the water column, sediment trap and Pb-210 based accumulation rates for Mn and Fe indicate that the burial rate of Mn and Fe below the diagenetic Mn-Fe oxide zone is not distinguishably different from the lakewide retention rate. The concentrations of Mn and Fe presently in crusts may be at steady state.

The diagenetic oxides represent concentrations of metals on a lakewide basis equivalent to metal accumulation of 1450 yr for Mn and 225 yr for Fe (Table 7-1). If Toolik Lake is 12,000 yr old, only 12% of Mn and 2% of acid reducible Fe has been retained as diagenetically mobile oxides over the course of the lake's existence.

If the Mn crusts were increasing in size, the rate of Fe(III) reduction would decrease because a higher fraction of organic matter oxidation would occur in conjunction with Mn reduction. Eventually, this would mean that Fe reduction should be suppressed, and that Mn(IV) would be the only significant organic matter oxidant other than dissolved oxygen in these sediments. For this to occur, no important

removal processes for  $\text{Mn}^{2+}$  should be present. Manganese burial in reducing sediments suggests that some mechanism is retaining  $\text{Mn(II)}$  in the solid phase. Pore water  $\text{Mn}^{2+}$  burial is not a quantitatively important process in these sediments ( $\ll 0.1 \text{ mmole m}^{-2} \text{ yr}^{-1}$ ). In Chapter 5, the removal of  $\text{Mn}^{2+}$  as carbonates and phosphates was considered, but their importance or lack thereof was not proven. Figure 7-4 shows the relationship between dissolved and particulate Mn beneath the Mn and Fe enriched zones. The importance of this relationship is that the burial rate of solid phase Mn below the crusts is higher when pore water  $\text{Mn}^{2+}$  concentrations are higher. A limit on the concentration of  $\text{Mn}^{2+}$  may occur by formation of solid phase Mn compounds. If this is the case, the growth of Mn crusts may be limited by the rate of removal of porewater  $\text{Mn}^{2+}$ , assuming constant water column inputs of Mn to the interface.

The growth of Fe crusts beneath Mn crusts and in the absence of Mn crusts may have similar limits. If  $\text{Fe(III)}$  is the electron acceptor for the final stages of organic matter oxidation, the size of the diagenetic enrichments may be a function of organic matter input and the extent of organic C oxidation via energetically more favored electron acceptors (dissolved oxygen and  $\text{Mn(IV)}$ ).

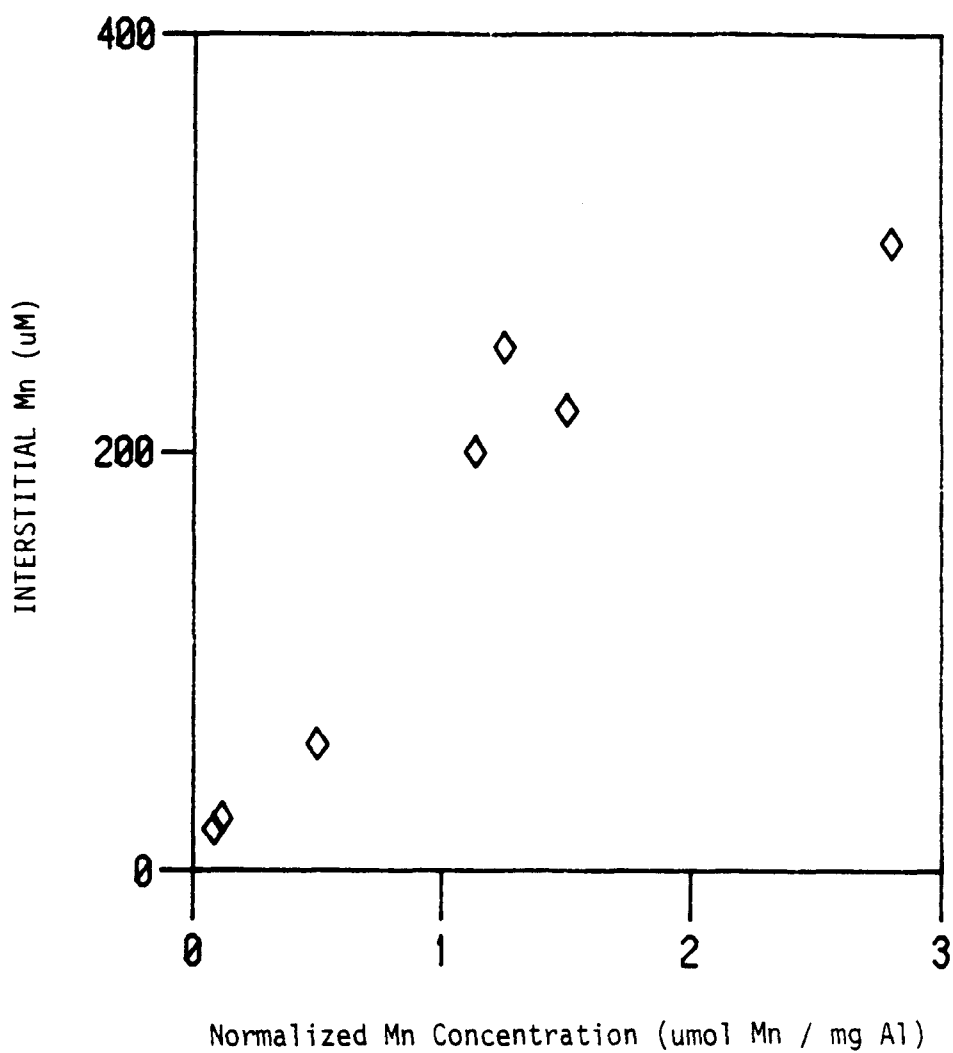


Figure 7-4. Dissolved  $\text{Mn}^{2+}$  versus the concentration of solid phase Mn (normalized to Al). These two parameters are significantly correlated ( $r=0.924$ ,  $p<0.01$ ).

### THE TOOLIK LAKE PHOSPHORUS CYCLE

A P budget constructed with the same terms as those in the Mn and Fe budget is shown in Figure 7-5. The Pb-210 sedimentation rates have been combined with an estimated background P concentration to obtain P burial rates. Estimates of the concentrations of P which are buried can be subjective and large errors may be possible in some cores. The important features of the P cycle in Toolik Lake are:

1. Approximately 44% of the yearly PP input and 26% of the yearly TDP input enters the lake in the first 10% of summer flow.
2. The retention of P by Toolik Lake (in 1980) is only 28% of the total input rate.
3. The P loading rate (influx of P to the lake) is 2 to 4 mmol m<sup>-2</sup> yr<sup>-1</sup>, a value similar to other oligotrophic lakes.
4. Conversion of unreactive P to reactive species usable by phytoplankton is an important process in Toolik Lake.
5. Comparison of the estimated retention of P in Toolik Lake based on sediment traps and the stream budget show excellent agreement. Lead-210 derived rates are 67% higher. The difference may be an incomplete determination of total P by the persulfate oxidation method.
6. The rate of migration of inorganic P within Toolik Lake sediment is similar to the input rate terms. This flux is smaller relative to the overall P cycle than the equivalent process is for the Mn and Fe cycles.
7. Diffusion of pore water PO<sub>4</sub> out of sediments is a minor process in

# PHOSPHORUS

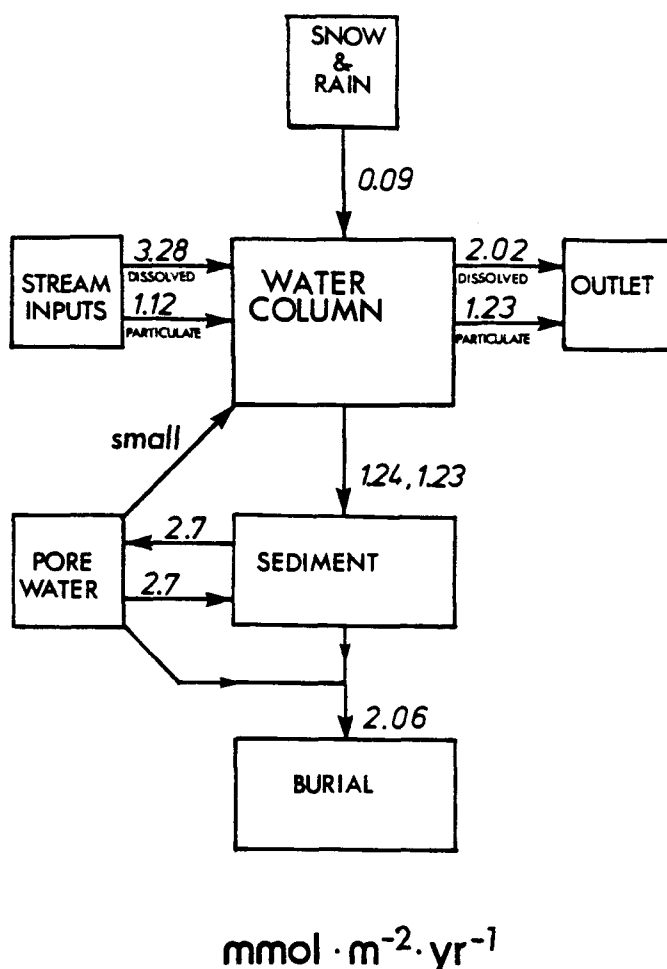


Figure 7-5. Phosphorus cycle for Toolik Lake. All fluxes are normalized to the area of the lake. Two rates of P flux from the water column to sediment are included, the first ( $1.24 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) coming from the 1980 stream budget and the second ( $1.23 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) coming from sediment traps in 1981. The P burial rate ( $2.06 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) is from the Pb-210 derived sedimentation rates.

these sediments; retention of phosphate by Fe(III) oxyhydroxides limits migration into the water column.

8. Two modes of Fe-P association occur in these sediments: adsorbed complexes and authigenic vivianite.

#### SUMMARY OF MAJOR FINDINGS

In a wide ranging study such as this, it is sometimes difficult for the reader to sort out the major findings from the detail involved in the study of major processes. The overall cycles of Mn, Fe and P have been discussed in this chapter and the most important findings of this overall project are:

1. A large proportion (>25%) of the yearly input of PP, TDP, DMn, POC, K and suspended solids enter Toolik Lake via streams during the first 10% of the summer flow season.
2. The daily removal rate of Mn and Fe from the Toolik Lake water-column is correlated with the daily rate of primary production and the sedimentation of N and P, suggesting that regulation of metal concentrations in the water column has an important biological component.
3. The mineralization of stream organic P is an important process, and may be significant in the regulation of primary production in Toolik Lake.
4. The calculation of sedimentation rates of total Mn, acid reducible Fe and total P via three independent techniques (stream budget, sediment traps and sediment accumulation) yields reasonably consistent results.



5. Sedimentation rates and the flux of Pb-210 to the sediment are among the lowest on record.
6. Manganese and Fe crusts and enrichments in sediment near the interface can contain up to 22% Mn and 26% Fe by weight, a result of a redox driven reduction/diffusion/oxidation cycle which maintains high concentrations of solid phase Mn and Fe within oxidizing horizons.
7. Organic rich littoral sediments have less solid phase Mn than profundal sediments, a result of the more reducing conditions found in the littoral zone.
8. The distribution of pore water  $\text{PO}_4$  is controlled by four processes: diffusion, adsorption to and desorption from Fe(III) oxyhydroxides, and the formation of authigenic vivianite.
9. The geochemical distributions of Ra-226, Co, Ba, Ni, Mo, Ca, organic C and carbonates in the metal oxide rich zones of Toolik Lake sediment are strongly affected by the diagenetic redistribution of Mn and Fe and distinct enrichments in these sediment components are found in oxidized horizons.

### SUGGESTIONS FOR FUTURE RESEARCH

In any project of this size, numerous opportunities for future research are made apparent to those close to the work. The main emphasis of this research has been the use of different techniques to create detailed mass balances of Mn, Fe and P in sediments and the water column of an arctic lake. It has allowed me to understand the fluxes of numerous elements in this ecosystem in more detail than possible in previous studies. Inferences on the nature of the processes occurring are made on the basis of measurements of both concentrations and fluxes. These inferences form the basis of a first step at understanding the chemical ecology of arctic lakes and the geochemistry of post-oxic sediments.

The next step in the understanding of arctic lake and diagenetic processes lies in the experimental measurement and examination of individual processes. My work has raised more questions about processes than I have answered, but at the very least, the mass balance approach allows an investigator to know what the quantitatively important processes in elemental cycles are. Specific recommendations for future research are:

1. Early season DMn fluxes: the processes which result in high concentrations of DMn in early season stream flow are not understood.
2. Water column Mn removal: a biological control mechanism of water column Mn concentrations has been suggested in this study; tracer experiments could better define the processes at work.
3. The nature of Mn and Fe solids: determination of the valence and

mineralogical forms of particulate Mn and Fe both in the water column and in sediments could provide clues about the nature of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  binding and oxidation.

4. Manganese oxidation and reduction in sediments: tracer experiments on the influence of biotic and abiotic processes on Mn phase changes should be performed, with an emphasis on the interaction of Mn(IV) and  $\text{Fe}^{2+}$  in aquatic sediments.

5. Removal of metals as oxides, phosphates and carbonates: the application of the electron microprobe and similar techniques to these sediments could reveal fine structure in the distribution of major and minor elements and elucidate important mineral-forming processes.

6. Watershed nutrient balance: the small watershed concept (Likens et al., 1977) has not been fully exploited in arctic studies, despite the short stream flow season and impermeable nature of frozen soils. Cooperative efforts between aquatic scientists and terrestrial ecologists could form the basis for a more complete understanding of nutrient cycling and ecosystem development in the Arctic.

## REFERENCES

- Aller, R.C. 1980a. Diagenetic processes near the sediment-water interface of Long Island Sound I. Decomposition and nutrient element geochemistry (S,N,P). Adv. Geophys. 22:237-350.
- Aller, R.C. 1980b. Diagenetic processes near the sediment-water interface of Long Island Sound II. Fe and Mn. Adv. Geophys. 22:351-415.
- Alexander, V., and R.J. Barsdate. 1971. Physical limnology, chemistry and plant productivity of a taiga lake. Int. Rev. Gesamten Hydrobiol. 56:825-872.
- Alexander, V.A., and R.J. Barsdate. 1974. Limnological studies of a subarctic lake system. Int. Rev. Gesamten Hydrobiol. 59:737-753.
- American Public Health Association. 1975. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, N.Y.
- Armstrong, F.A.J., C.R. Stearns and J.D.H. Strickland. 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon AutoAnalyzer and associated equipment. Deep-Sea Res. 14:381-389.
- Barsdate, R.J., and V. Alexander. 1971. Geochemistry and primary productivity of the Tangle Lake system, an Alaskan alpine watershed. Arct. Alp. Res. 3:27-41.
- Barsdate, R.J., and W.R. Matson. 1966. Trace metals in arctic and subarctic lakes with references to the organic complex of metals. In: Radioecol. Conc. Processes Proc. Int. Symp., 1966.
- Berner, R.A. 1976. Inclusion of adsorption in the modelling of early diagenesis. Earth Planet. Sci. Lett. 29:333-340.
- Berner, R.A. 1980. Early Diagenesis: a Theoretical Approach. Princeton Univ. Press.
- Berner, R.A. 1981. A new geochemical classification of sedimentary environments. J. Sediment. Petrol. 51:359-365.
- Bray, J.T. 1973. The behavior of phosphate in the interstitial waters of Chesapeake Bay sediments. Ph.D. dissertation. Johns Hopkins Univ. 149 p.

- Brown, J., and R.L. Berg,. 1980. Environmental engineering and ecological baseline investigations along the Yukon River-Prudhoe Bay Haul Road. CRREL Report 80-19. 203 p.
- Bortleson, G.C., and G.F. Lee. 1974. Phosphorus, iron and manganese distribution in sediment cores of six Wisconsin lakes. Limnol. Oceanogr. 19:794-801.
- Bruland, K.W., K. Bertine, M. Koide and E.D. Goldberg. 1973. History of metal pollution in Southern California coastal zone. Environ. Sci. Technol. 5:425-432.
- Brunskill, G.J., D. Povoledo, B.W. Graham and M.P. Stainton. 1971. Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Board Can. 28:277-294.
- Brunskill, G.J., D.M. Rosenberg, N.B. Snow, G.L. Vascotto and R.W. Wagemann. 1973. Ecological studies of aquatic systems in the MacKenzie-Porcupine drainages in relation to proposed pipeline and highway developments. Canada Task Force N. Oil Dev. Env. Soc. Comm. Vol. II. Report 73-41. 345 p.
- Buchanan, C.L. 1978. Arctic investigations of some factors that control the vertical distributions and swimming activities of zooplankton. Ph.D. dissertation, Univ. of New Hampshire. 103 p.
- Burdige, D.J. 1983. The biogeochemistry of manganese redox reactions: rates and mechanisms. Ph.D. dissertation, Univ. of California at San Diego. 251 p.
- Burdige, D.J., and J.M. Gieskes. 1983. A pore water/solid phase diagenetic model for manganese in marine sediments. Am. J. Sci. 283:29-47.
- Calvert, S.E. and N.B. Price. 1972. Diffusion and reaction profiles of dissolved manganese in the porewaters of marine sediments. Earth Planet Sci. Lett. 16:245-249.
- Calvert, S.E. and N.B. Price. 1977. Shallow water, continental margin and lacustrine nodules: distributions and geochemistry. In: G.P. Glasby (ed.), Marine Manganese Deposits. Elsevier, Amsterdam.
- Carignan, R., and R.J. Flett. 1981. Post depositional mobility of phosphorus in lake sediments. Limnol. Oceanogr. 26:361-366.
- Chapnick, S.D., W.S. Moore and K.H. Nealson. 1982. Microbially mediated manganese oxidation in a freshwater lake. Limnol. Oceanogr. 27:1004-1014.

- Coakley, J.P., and B.R. Rust. 1968. Sedimentation in an arctic lake. J. Sediment. Petrol. 38:1290-1300.
- Cook, R.B. 1981. The biogeochemistry of sulfur in two small lakes. Ph.D. dissertation, Columbia Univ. 234 p.
- Cuker, B.E. 1983. Grazing and community interactions in controlling the activity and composition of the epilithic algal community of an arctic lake. Limnol. Oceanogr. 28:133-141.
- Davis, J.A., and J.O. Leckie. 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12:1309-1315.
- Davison, W. 1979. Soluble inorganic ferrous complexes in natural waters. Geochim. Cosmochim. Acta. 43:1693-1696.
- Davison, W., C. Woof and E. Rigg. 1982. The dynamics of iron and manganese in a seasonally anoxic lake; direct measurement using sediment traps. Limnol. Oceanogr. 27:987-1003
- Davison, W., and G. Seed. 1983. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. Geochim. Cosmochim. Acta. 47:67-79.
- Dean, W.E., and P.E. Greeson. 1979. Influences of algae on the formation of freshwater manganese nodules, Oneida Lake, New York. Arch. Hydrobiol. 86:181-192.
- Dean, W.E., W.S. Moore and K.H. Nealson. 1981. Manganese cycles and the origin of manganese nodules, Oneida Lake, New York, U.S.A. Chem. Geol. 34:53-64.
- Delfino, J.J., G.C. Bortleson and G.F. Lee. 1969. Distribution of Mn, Fe, P, Mg, K, Na and Ca in the surface sediments of Lake Mendota, Wisconsin. Environ. Sci. Technol. 8:1189-1192.
- de March, L. 1975. Nutrient budgets for a high arctic lake (Char Lake, N.W.T.). Verh. Int. Ver. Theor. Angew. Limnol. 19:496-503.
- de March, L. 1978. Permanent sedimentation of nitrogen, phosphorus and organic carbon in a high arctic lake. J. Fish. Res. Board Can. 35:1089-1094.
- Dillon, P.J., and W.B. Kirchner. 1975. The effects of geology and land use on the export of phosphorus from watersheds. Water Res. 9:135-148.

- Edgington, D.N., and J.A. Robbins. 1976. Records of lead deposition in Lake Michigan sediments since 1800. Environ. Sci. Technol. 10:266-274.
- Ehrlich, H.L. 1981. Geomicrobiology. Marcel Dekker, N.Y.
- Elder, J.F. 1975. Complexation side reactions involving trace metals in natural water systems. Limnol. Oceanogr. 20:96-102.
- Emerson, S. 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochim. Cosmochim. Acta. 40:925-934.
- Emerson, S., and G. Widmer. 1978. Early diagenesis in anaerobic lake sediments II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. Geochim. Cosmochim. Acta. 34:1307-1316.
- Emerson, S., R.E. Cranston and P.S. Liss. 1979. Redox species in a reducing fjord; equilibrium and kinetic considerations. Deep-Sea Res. 26A:859-873.
- Emerson, S., S. Kalhorn, L. Jacobs, B.M. Tebo, K.H. Nealson and R.A. Rosson. 1982. Environmental oxidation rate of manganese(II): bacterial catalysis. Geochim. Cosmochim. Acta. 46:1073-1079.
- Evans, J.E., T.C. Johnson, E.C. Alexander, Jr., R.S. Lively and S.J. Eisenreich. 1981. Sedimentation rates and depositional processes in Lake Superior from Pb-210 geochronology. J. Great Lakes Res. 7:299-310.
- Evans, R.D., and F.H. Rigler. 1980a. The measurement of whole lake sediment accumulation and phosphorus retention using lead-210 dating. Can. J. Fish. Aquat. Sci. 37:817-822.
- Evans, R.D., and F.H. Rigler. 1980b. Calculation of the total anthropogenic lead in the sediments of a rural Ontario lake. Environ. Sci. Technol. 14:216-218.
- Evans, R.D., and F.H. Rigler. 1983. A test of lead-210 dating for the measurement of whole lake soft sediment accumulation. Can. J. Fish. Aquat. Sci. 40:506-515.
- Farmer, F.G. 1978. The determination of sedimentation rates in Lake Ontario using the Pb-210 dating method. Can. J. Earth Sci. 15:431-437.

- Federle, T.W. 1981. The processes and control of the microbial colonization of plant litter in an arctic lake. Ph.D. dissertation, Univ. of Cincinnati. 133 p.
- Fenchel, T., and T.H. Blackburn. 1979. Bacteria and Mineral Cycling. Academic Press, N.Y.
- Forstner, U., and G.T.W. Wittman. 1979. Metal Pollution in the Aquatic Environment. Springer Verlag, Berlin.
- Froelich, P.N., G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartmann and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta. 43:1075-1090.
- Gadde, R.R., and H.A. Laitinen. 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. Anal. Chem. 46:2022-2026.
- Gibb, M.M. 1979. A simple method for the rapid determination of iron in natural waters. Water Res. 13:295-297.
- Gibbs, R.J. 1977. Transport phases of transition metals in the Amazon and Yukon Rivers. Geol. Soc. Am. Bull. 88:829-843.
- Giovanolli, R., P. Burki, M. Giaffredi and W. Stumm. 1975. Layer structured manganese oxide hydroxides IV. The buserite group: structure stabilization by transition elements. Chimia 29:517-520.
- Gorham, E., and D.J. Swaine. 1965. The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. Limnol. Oceanogr. 10:268-279.
- Hamilton, T.D., and S.C. Porter. 1975. Itkillik glaciation in the Brooks Range, northern Alaska. Quat. Res. 5:471-497.
- Hem, J.D. 1978. Redox processes at surfaces of manganese oxide and their effects on aqueous metal ions. Chem. Geol. 21:199-218.
- Hem, J.D. 1980. Redox coprecipitation mechanism of manganese oxides. In: Kavanaugh and Leckie (eds.), Particulates in water. Adv. in Chem. Series 189. American Chemical Society, Washington, D.C.
- Hesslein, R.H. 1976. The fluxes of CH<sub>4</sub>, CO<sub>2</sub> and NH<sub>3</sub>-N from sediments and their subsequent redistribution in a small lake. Ph.D. dissertation, Columbia Univ. 185 p.



- Hobbie, J.E. 1973. Arctic limnology: a review. In: M.E. Britton, (ed.), Alaskan Arctic Tundra. Arct. Inst. North Amer. Tech. Pap. 25.
- Hobbie, J.E., (ed.), 1980. Limnology of Tundra Ponds, Barrow, Alaska. Dowden, Hutchinson and Ross, Stroudsburg.
- Hobbie, J.E., T.L. Corliss and B.J. Peterson. 1983. Seasonal patterns of bacterial abundance in an arctic lake. Arct. Alp. Res. 15:253-259.
- Holdren, G.C. 1977. Factors affecting phosphorus release from lake sediments. Ph.D. dissertation, Univ. of Wisconsin-Madison. 172 p.
- Holdren, G.R. 1977. Distribution and behavior of manganese in the interstitial waters of Chesapeake Bay sediments during early diagenesis. Ph.D. dissertation, Johns Hopkins Univ. 190 p.
- Jacobsen, R.L., and D. Langmuir. 1974. Dissociation constants of calcite and  $\text{CaHCO}_3^+$  from 0 to 50°C. Geochim. Cosmochim. Acta. 38:301-318.
- Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: Trace inorganics in water. Adv. Chem. Ser. 73. American Chemical Society, Washington, D.C.
- Jones, B.F., and C.J. Bowser. 1978. The mineralogy and related chemistry of lake sediments. In: A. Lerman, (ed.), Lakes: Chemistry, Geology, Physics. Springer Verlag, N.Y.
- Kalff, J. 1968. Some physical and chemical characteristics of arctic freshwaters in Alaska and northwestern Canada. J. Fish. Res. Board Can. 25:2575-2587.
- Kalff, J. 1971. Nutrient limiting factors in an arctic tundra pond. Ecology 52:655-659.
- Kelley, C.A., J.W.M. Rudd, R.B. Cook and D.W. Schindler. 1982. The potential importance of bacterial processes in regulating rate of lake acidification. Limnol. Oceanogr. 27:868-882.
- Kelts, K., and K.J. Hsu. 1978. Freshwater carbonate sedimentation. In: A. Lerman, (ed.), Lakes: Chemistry, Geology, Physics. Springer Verlag, N.Y.
- Kinney, P.J., D.M. Schell, V. Alexander, D.C. Burrell, R. Cooney and A.S. Naidu. 1972. Baseline data study of an Alaskan arctic environment. Univ. Alaska. Inst. Mar. Sci. Rep. R-72-3. 275 p.

- Kirchner, W.B. 1975. An evaluation of sediment trap methodology. Limnol. Oceanogr. 20:657-660.
- Kipphut, G.K. 1978. An investigation of sedimentary processes in lakes. Ph.D. dissertation, Columbia Univ. 179 p.
- Klingensmith, K.L. 1981. Sediment nitrification, denitrification and nitrous oxide production in an arctic lake. M.S. thesis, Univ. of Alaska, Fairbanks. 60 p.
- Koide, M., A. Soutar and E.D. Goldberg. 1972. Marine geochronology with Pb-210. Earth Planet. Sci. Lett. 14:442-446.
- Kramer, J.R. 1964. Theoretical model for the chemical composition of freshwater with application to the Great Lakes. Univ. Mich. Great Lakes Res. Div. Publ. 11:147-160.
- Krauskopf, K.B. 1957. Separation of manganese from iron in sedimentary processes. Geochim. Cosmochim. Acta. 12:61-68.
- Krishnaswami, S., and W.S. Moore. 1973. Accretion rates of freshwater manganese deposits. Nature 243:114-116.
- Krishnaswami, S., and D. Lal. 1978. Radionuclide limnology. In: A. Lerman, (ed.), Lakes: Chemistry, Geology, Physics. Springer Verlag, N.Y.
- Krom, M.D., and R.A. Berner. 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochim. Cosmochim. Acta. 45:207-216.
- Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. In: P.A. Krenkel, (ed.), Heavy Metals in the Aquatic Environment. Pergamon Press, N.Y.
- Lerman, A. 1979. Geochemical Processes: Water and Sediment Environments. Wiley, N.Y.
- Li, Y.-H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta. 38:703-714.
- Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton and N.M. Johnson. 1977. Biogeochemistry of a Forested Ecosystem. Springer Verlag, N.Y.
- Loder, T.C. 1971. Distribution of dissolved and particulate organic carbon in Alaskan polar, sub-polar and estuarine waters. Ph.D. dissertation, Univ. of Alaska, Fairbanks. 236 p.

- McCaffrey, R.J., A.C. Myers, E. Davey, G. Morrison, M. Bender, N. Luedtke, D. Cullen, P. Froelich and G. Klinkhammer. 1980. The relation between porewater chemistry and benthic fluxes in Narragansett Bay, Rhode Island. Limnol. Oceanogr. 25:31-44.
- McCammon, C.A., and R.G. Burns. 1980. The oxidation mechanism of vivianite as studied by Mossbauer spectroscopy. Am. Mineral. 65:361-366.
- Medlin, J.H., N.H. Suhr and J.B. Bodkin. 1969. Atomic absorption analysis of silicates employing  $\text{LiBO}_2$  fusion. At. Abs. Newsl. 8:25-29.
- Mellor, J.C. 1982. Bathymetry of Alaskan arctic lakes: a key to resource inventory with remote sensing methods. Ph.D. dissertation, Univ. of Alaska, Fairbanks. 342 p.
- Menzel, D.W., and N. Corwin. 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. Limnol. Oceanogr. 17:58-67.
- Miller, M.C., V. Alexander and R.J. Barsdate. 1978. The effect of oil spills on phytoplankton in an arctic lake and ponds. Arctic 31:192-218
- Miller, M.C., G.R. Hater, P. Spatt, P. Westlake and D. Yeakel. 1983. Primary production and its control in Toolik Lake, Alaska. Unpublished manuscript, Univ. of Cincinnati.
- Mortimer, C.H. 1971. Chemical exchanges between sediments and water in the Great Lakes - speculations on probable regulatory mechanisms. Limnol. Oceanogr. 16:387-404.
- Mulholland, P.J. and J.A. Watts. Transport of organic carbon to the oceans by rivers of North America: a synthesis of existing data. Tellus 34:176-186.
- Morgan, J.J. 1967. Chemical equilibria and kinetic properties of manganese in natural waters. In: S.D. Faust and J.V. Hunter, (eds.), Principles and Application of Water Chemistry. John Wiley, N.Y.
- Murray, J.W. 1975. The interaction of metal ions at the manganese dioxide solution interface. Geochim. Cosmochim. Acta. 39:505-519.
- Murray, J.W., and G. Gill. 1978. The geochemistry of iron in Puget Sound. Geochim. Cosmochim. Acta. 42:9-19.
- Murray, J.W., and V. Grundmanis. 1980. Oxygen consumption in pelagic marine sediments. Science 209:1527-1530.

- Murray, J.W., V. Grundmanis and W.M. Smethie, Jr. 1979. Interstitial water chemistry in the sediments of Saanich Inlet. Geochim. Cosmochim. Acta. 42:1011-1026.
- Nicholls, K.H., and P.J. Dillon. 1978. An evaluation of phosphorus-chlorophyll-phytoplankton relationships for lakes. Int. Rev. Gesamten Hydrobiol. 63:141-154.
- Nriagu, J.O., 1972. Stability of vivianite and ion pair formation in the system  $\text{Fe}_3(\text{PO}_4)_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ . Geochim. Cosmochim. Acta. 36:454-470.
- Nriagu, J.O. and C.I. Dell. 1974. Diagenetic formation of iron phosphates in recent lake sediments. Am. Mineral. 59:934-946.
- O'Brien, W.J., C. Buchanan and J.F. Haney. 1979. Arctic zooplankton community structure: exceptions to some general rules. Arctic 32:237-247.
- Personn, G., S.K. Holmgren, M. Jansson, A. Lundgren, B. Nyman, D. Solander and C. Anell. 1975. Phosphorus and nitrogen and the regulation of lake ecosystems: experimental approaches in subarctic Sweden. In: Proc. Circumpolar Conf. North. Ecol. Ottawa.
- Prentki, R.T. 1976. Phosphorus cycling in tundra ponds. Ph.D. dissertation, Univ. of Alaska. 275 p.
- Prentki, R.T., M.C. Miller, R.J. Barsdate, V. Alexander, J. Kelley and P. Coyne. 1980. Chemistry. In: J.E. Hobbie, (ed.), Limnology of Tundra Ponds, Barrow, Alaska. Dowden, Hutchinson and Ross. Stroudsburg.
- Raad, A.T., R. Protz and R.L. Thomas. 1969. Determination of Na-dithionate and  $\text{NH}_4$ -oxalate extractable Fe, Al and Mn in soils by atomic absorption spectrophotometry. Can. J. Soil Sci. 49:89-94.
- Reeburgh, W.S. 1967. An improved interstitial water sampler. Limnol. Oceanogr. 12:163-165.
- Reeburgh, W.S. 1983. Rates of biogeochemical processes in anoxic sediments. Ann. Rev. Earth Planet. Sci. 11:269-298.
- Rigler, F.H. 1978a. Limnology in the high Arctic: a case study of Char Lake. Verh. Int. Ver. Theor. Angew Limnol. 20:127-140.
- Rigler, F.H. 1978b. Passage of phosphorus through a catchment. In: W.E. Krumbein, (ed.), Environmental Biogeochemistry and Geomicrobiology. Ann Arbor Science.

- Robbins, J.A. 1978. Geochemical and geophysical applications of radioactive lead. In: J.O. Nriagu, (ed.), The Biogeochemistry of Lead in the Environment. Flsevier/North Holland, Amsterdam.
- Robbins, J.A., and E. Callender. 1975. Diagenesis of manganese in Lake Michigan sediments. Am. J. Sci. 275:512-533.
- Robbins, J.A., and D.N. Edgington. 1975. Determination of sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochim. Cosmochim. Acta. 39:285-304.
- Robbins, J.A., J.R. Krezoski and S.C. Mozley. 1977. Radioactivity in sediments of the Great Lakes: post depositional redistribution by deposit feeding organisms. Earth Planet. Sci. Lett. 36:325-333.
- Robbins, J.A., D.N. Edgington and A.L.W. Kemp. 1978. Comparative Pb-210, Cs-137 and pollen geochronologies of sediments from Lakes Ontario and Erie. Quat. Res. 10:256-278.
- Schindler, D.W., H.E. Welch, J. Kalff, G.J. Brunskill and N. Kritsch. 1974a. Physical and chemical limnology of Char Lake, Cornwallis Island. J. Fish. Res. Board Can. 31:587-607.
- Schindler, D.W., J. Kalff, H.E. Welch, G.J. Brunskill, H. Kling and N. Kritsch. 1974b. Eutrophication in the high arctic-Meretta Lake, Cornwallis Island. J. Fish. Res. Board Can. 31:647-662.
- Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong and R.F. Harris. 1971. Sorption of inorganic phosphates by lake sediments. Soil Soc. Am. Proc. 35:244-249.
- Slawyk, G., and J.J. MacIsaac. 1972. Comparison of two automated ammonium methods in a region of coastal upwelling. Deep-Sea Res. 19:521-524.
- Sorenson, J. 1982. Reduction of ferric iron in anaerobic marine sediment and interaction with reduction of nitrate and sulfate. Appl. Environ. Microbiol. 43:319-324.
- Sozanski, A.G., and D.S. Cronan. 1979. Ferromanganese concretions in Shebandowan Lakes, Ontario. Can. J. Earth Sci. 16:126-140.
- Stainton, M.P. 1973. A syringe gas stripping procedure for gas chromatographic determination of dissolved inorganic and organic carbon in freshwater and carbonates in sediments. J. Fish. Res. Board Can. 30:1441-1445.
- Stainton, M.P. 1980. Errors in molybdenum blue methods for determining orthophosphate in freshwater. Can. J. Fish. Aquat. Sci. 37:472-478.

- Stone, A.T. 1983. The reduction and dissolution of Mn(III) and Mn(IV) oxides by organics. Ph.D. dissertation, California Institute of Technology. 302 p.
- Strakhov, N.M. 1966. Types of manganese accumulation in present-day basins: their significance in understanding of manganese mineralization. Internat. Geol. Rev. 8:1172-1196.
- Strickland, J.D.H., and T.R. Parsons. 1968. A Practical Handbook for Seawater Analysis. Fish. Res. Board Can. Bull. 167. Ottawa.
- Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. Wiley Interscience. 780 p.
- Sugai, S.F., and D.C. Burrell. 1983. Transport of dissolved organic carbon, nutrients and trace metals from the Wilson and Blossom Rivers to Smeaton Bay, southeast Alaska. In: D.C. Burrell, P.I. Transport and reaction of heavy metals in Alaskan fjord estuaries. Unpublished Univ. of Alaska Inst. Marine Sci. Rep. to U.S. DOE.
- Sung, W. and J.J. Morgan. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ. Sci. Technol. 5:561-568.
- Syers, J.K., R.F. Harris and D.E. Armstrong. 1973. Phosphate chemistry in lake sediments. J. Environ. Quality. 2:1-14.
- Tessenow, U. 1974. Lösungs-, diffusions- und sorptionsprozesse in der Oberschicht von Seesedimenten. Arch. Hydrobiol. Suppl. 47:1-79.
- Tessenow, U., and Y. Baynes. 1975. Redox dependant accumulation of Fe and Mn in a littoral sediment supporting *Isoetes lacustris* l. Naturwissenschaften 62:342-343
- Tessenow, U., and Y. Baynes. 1978. Redoxchemische einflüsse von *Isoetes lacustris* L. im littoral sediment des Feldsees. Arch Hydrobiol. 82:20-48.
- Tipping, E. 1981. Adsorption by goethite of humic substances from three different lakes. Chem. Geol. 33:81-89.
- Trefry, J.H., and B.J. Presley. 1982. Manganese fluxes from Mississippi Delta sediments. Geochim. Cosmochim. Acta. 46:1715-1726.
- Tsunogai, S., I. Yonemaru and M. Kusakabe. 1979. Post depositional migration of Cu, Zn, Ni, Co, Pb and Ba in deep sea sediments. Geochem. J. 13:239-252.

- Ullman, W.J., and R.C. Aller. 1982. Diffusion coefficients in near-shore marine sediments. Limnol. Oceanogr. 27:552-556.
- U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency. Washington, D.C.
- Vallentyne, J.R. 1973. The algal bowl, a Faustian view of eutrophication. F. Am. Soc. Exp. Biol. Proc. 32:1754-1757.
- Verdouw, H., and E.M.J. Dekkers. 1980. Iron and manganese in Lake Vechten (The Netherlands); dynamics and role in the cycle of reducing power. Arch. Hydrobiol. 89:509-532.
- Vollenweider, R.A. 1976. Rotsee, a source, not a sink for phosphorus? Hydrobiologie. 38:29-34.
- von Rosenberg, D. 1969. Methods for the Numerical Solution of Partial Differential Equations. Elsevier, N.Y.
- Watanabe, I., and C. Furusaka. 1980. Microbial ecology of flooded rice soils. In: M. Alexander, (ed.), Advances in Microbial Ecology, Vol. 4. Plenum Press, N.Y.
- Wetzel, R.G. 1975. Limnology. Saunders, Philadelphia. 743 p.
- Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris and D.E. Armstrong. 1971. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Environ. Sci. Technol. 5:1113-1120.
- Williams, J.D.H., J.M. Jaquet and R.L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33:413-429.
- Yoshida, K., and T. Kamura. 1975. The reduction mechanism of manganese in paddy soils. VII. Model experiments on the role of ferrous iron in manganese reduction. Nippon Dojohiryo Gaku Zasshi. 46:382-388.

- Ullman, W.J., and R.C. Aller. 1982. Diffusion coefficients in near-shore marine sediments. Limnol. Oceanogr. 27:552-556.
- U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency. Washington, D.C.
- Vallentyne, J.R. 1973. The algal bowl, a Faustian view of eutrophication. F. Am. Soc. Exp. Biol. Proc. 32:1754-1757.
- Verdouw, H., and E.M.J. Dekkers. 1980. Iron and manganese in Lake Vechten (The Netherlands); dynamics and role in the cycle of reducing power. Arch. Hydrobiol. 89:509-532.
- Vollenweider, R.A. 1976. Rotsee, a source, not a sink for phosphorus? Hydrobiologie. 38:29-34.
- von Rosenberg, D. 1969. Methods for the Numerical Solution of Partial Differential Equations. Elsevier, N.Y.
- Watanabe, I., and C. Furusaka. 1980. Microbial ecology of flooded rice soils. In: M. Alexander, (ed.), Advances in Microbial Ecology, Vol. 4. Plenum Press, N.Y.
- Wetzel, R.G. 1975. Limnology. Saunders, Philadelphia. 743 p.
- Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris and D.E. Armstrong. 1971. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Environ. Sci. Technol. 5:1113-1120.
- Williams, J.D.H., J.M. Jaquet and R.L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33:413-429.
- Yoshida, K., and T. Kamura. 1975. The reduction mechanism of manganese in paddy soils. VII. Model experiments on the role of ferrous iron in manganese reduction. Nippon Dojohiryo Gaku Zasshi. 46:382-388.



## APPENDIX A. STREAM AND WATER COLUMN DATA

The data in this appendix are:

1. 1976-1978 water column chemistry: P and major cations.
2. Dissolved oxygen concentrations.
3. Sediment trap fluxes.
4. 1980 main station water chemistry.
5. 1977 and 1978 stream chemistry.
6. 1980 stream chemistry.
7. 1981 stream chemistry.

All concentrations are  $\mu\text{M}$  unless otherwise noted. The suspended load concentrations (WT) are  $\text{mg l}^{-1}$ .

1976-1978 water column chemistry: P and major cations.

DEPTH	DATE	PP	TDP	DATE	PP	TDP	DATE	PP	TDP	DEPTH	DATE	PP	TDP	Na	K	Ca	Mg	DATE	PP	TDP	Na	K	Ca	Mg
0	08/29/76	0.07	0.20	09/17/76	0.15	0.17	10/02/76	0.17	0.26	0	02/12/78	----	----	----	----	----	----	03/25/78	----	----	----	----	----	----
1		0.09	0.20		0.15	0.20		0.15	0.22	1		0.09	0.19	40	9	290	60		0.13	0.22	36	9	288	63
3		0.09	0.09		0.18	0.19		0.19	0.17	3		0.08	0.16	33	8	230	58		0.14	0.14	31	8	230	57
5		0.10	0.16		0.17	0.12		0.16	0.18	5		0.07	0.30	28	6	218	53		0.18	0.14	33	9	246	60
8		0.09	0.11		0.15	0.41		0.18	0.21	8		0.08	0.22	30	7	222	56		0.13	0.10	23	7	209	53
12		0.11	0.15		0.14	0.47		0.16	0.21	12		0.07	----	30	7	216	54		0.09	0.11	27	7	214	53
16		0.10	0.15		0.19	0.23		----	----	16		0.08	0.28	26	6	203	49		0.11	0.10	31	7	215	53
0	10/24/76	0.15	0.46	12/09/76	----	----	02/26/77	----	----	0	04/21/78	----	----	----	----	----	----	05/21/78	----	----	----	----	----	----
1		0.15	0.30		0.18	0.43		0.15	0.16	1		0.13	----	28	8	236	59		0.08	0.18	37	9	240	59
3		0.11	0.22		0.17	0.44		0.07	0.16	3		0.12	----	26	8	230	58		0.07	0.19	57	9	240	68
5		0.13	0.22		0.15	0.19		0.13	0.08	5		0.07	----	27	7	217	54		0.07	0.22	23	7	277	55
8		0.09	0.63		----	----		0.15	0.08	8		0.06	0.19	24	7	217	54		0.06	0.18	23	8	233	58
12		0.08	0.33		----	----		0.11	0.09	12		0.06	----	28	7	218	55		0.06	0.16	31	8	285	58
16		0.09	0.16		----	----		0.11	0.09	16		0.09	0.12	23	7	215	53		0.05	0.20	20	7	265	57
0	04/04/77	----	----	05/12/77	----	----	05/22/77	----	----	0	06/03/78	----	----	----	----	----	----	07/20/78	0.12	0.12	----	----	----	----
1		0.10	0.12		0.20	0.13		----	0.11	1		0.06	0.15	5	2	24	3		0.15	----	----	----	----	----
3		0.19	0.10		0.26	0.11		----	0.09	3		0.15	0.26	15	11	179	45		0.08	0.10	----	----	----	----
5		0.28	0.05		0.22	0.09		----	0.14	5		0.11	0.24	24	11	211	56		0.09	0.09	----	----	----	----
8		0.12	0.05		0.15	0.08		----	0.11	8		0.07	0.24	21	8	220	55		0.10	----	----	----	----	----
12		0.11	----		0.16	0.12		----	0.06	12		0.08	0.32	20	9	216	55		0.11	0.10	----	----	----	----
16		0.12	0.05		0.13	0.09		----	0.10	16		0.07	0.33	37	8	294	56		0.13	0.11	----	----	----	----
0	07/01/77	0.13	0.18	08/01/77	0.06	0.35	08/21/77	0.06	0.50	0	07/31/78	----	0.16	18	7	176	45	09/01/78	0.10	0.14	18	7	----	----
1		0.19	0.16		0.10	0.14		0.07	----	1		0.06	----	----	----	----	----		0.11	0.16	16	6	----	----
3		0.14	0.18		0.11	----		0.08	0.16	3		0.07	----	27	7	182	45		0.09	0.11	16	6	----	----
5		0.14	0.19		0.09	0.12		0.04	0.30	5		0.07	0.13	17	7	176	45		0.09	0.14	17	7	----	----
8		0.11	0.22		0.11	0.10		0.07	----	8		0.07	0.11	18	7	175	45		0.09	0.11	20	7	----	----
12		0.09	0.21		0.11	0.09		0.10	0.13	12		0.09	0.11	18	8	172	44		0.10	0.32	17	7	----	----
16		----	----		----	----		0.07	----	16		0.10	0.11	17	8	172	44		0.12	0.13	20	7	----	----
0	09/14/77	0.09	0.11	10/25/77	0.08	0.26	11/20/77	0.06	0.26	0														
1		0.08	0.13		0.04	0.15		0.05	0.17	1														
3		0.06	0.13		0.07	0.15		0.06	0.16	3														
5		0.11	0.14		0.05	----		0.11	0.19	5														
8		0.08	0.12		0.08	0.17		0.09	----	8														
12		0.07	0.10		0.07	0.10		0.07	0.19	12														
16		0.09	0.15		0.06	0.15		0.06	0.11	16														

Dissolved oxygen concentrations, main station ( $\text{mg l}^{-1}$ ).

DEPTH	09/16/76	10/24/76	2/26/77	04/04/77	05/12/77	05/26/77
0	10.20	11.57	----	----	----	----
1	10.20	11.57	10.40	----	10.83	11.95
3	10.43	11.98	11.22	10.06	10.45	11.36
5	10.46	10.66	11.02	9.78	9.59	9.97
8	10.48	8.53	10.81	8.65	7.38	8.89
12	10.43	10.86	11.22	7.14	6.62	7.31
16	10.40	8.53	7.55	6.39	5.47	5.43

DEPTH	07/01/77	08/21/77	9/14/77	11/20/77	02/12/78	04/21/78
0	9.89	8.34	9.84	13.07	----	----
1	10.91	8.25	10.04	13.37	<b>13.40</b>	13.11
3	10.71	8.34	9.84	12.25	<b>12.53</b>	12.74
5	10.51	8.44	9.84	11.58	<b>11.55</b>	11.68
8	10.51	8.59	10.04	11.73	<b>10.91</b>	10.40
12	10.00	7.85	9.84	11.28	<b>9.91</b>	10.06
16	----	7.26	10.84	11.05	8.35	9.46

DEPTH	05/21/78	06/03/78	7/20/78	09/01/78
0	----	----	8.69	9.64
1	12.39	7.65	8.82	9.35
3	11.72	10.43	8.77	9.70
5	10.21	10.65	10.08	9.81
8	12.12	9.03	9.88	9.55
12	8.81	9.17	9.27	8.98
16	7.41	7.05	9.46	8.31

Sediment trap fluxes ( $\text{umol m}^{-2}\text{d}^{-1}$ ) from 1981.

TIME INTERVAL	P			Fe			Mn		
	A	B	$\bar{x}$	A	B	$\bar{x}$	A	B	$\bar{x}$
6/09-6/14	7.0	7.3	7.2	50	49	50	9.6	9.1	9.4
7/08-7/11	30.4	29.4	29.9	452	420	436	78.8	65.5	72.2
7/11-7/15	27.0	23.0	25.0	229	291	260	30.2	39.1	34.6
7/15-7/22	16.5	15.1	15.8	245	221	233	29.6	25.4	27.5
7/22-7/29	16.3	18.0	17.1	270	307	288	33.7	38.2	36.0
7/29-8/7	14.3	13.3	13.8	229	219	224	27.0	25.2	26.1
8/7-8/11	19.7	14.9	17.3	156	146	151	9.9	13.6	11.8
8/11-8/15	11.6	13.1	12.4	---	139	139	----	16.2	16.2
8/15-8/18	14.1	15.7	14.9	146	---	146	20.9	----	20.9
8/18-8/26	11.6	14.3	13.0	119	---	119	19.7	----	19.7
8/26-8/29	15.7	14.8	15.2	101	88	94	11.5	10.5	11.0

## 1980 Main station water chemistry.

DATE	DEPTH	PP	TDP	Na	K	Ca	Mg	POC	DOC	TFe	DFe	PMn	DMn	Si	WT	COLOR
05/13/80	1	0.06	0.26	12	3	69	20	11	267	----	0.07	0.007	0.286	9.1	0.88	0.10
	2	0.07	0.17	24	7	284	71	17	---	0.39	0.25	0.009	0.025	33.3	0.56	0.43
	4	0.07	0.07	25	8	279	70	15	533	0.32	0.27	0.016	0.016	32.6	0.34	0.44
	6	0.05	0.12	24	7	275	69	15	---	0.47	0.29	0.018	0.015	33.3	0.29	0.38
	8	0.05	0.09	23	7	270	68	10	592	0.45	0.30	0.022	0.018	36.6	0.18	0.48
	10	0.07	0.13	24	7	272	68	--	---	0.56	0.30	0.022	0.033	----	0.22	----
	12	0.06	0.12	25	9	277	70	9	467	0.56	0.30	0.033	0.022	38.0	0.19	----
	14	0.05	0.11	26	8	309	72	--	---	---	0.30	0.035	0.033	----	0.25	----
	16	0.06	0.15	24	7	279	70	10	---	0.61	0.30	0.044	0.031	36.6	0.18	0.36
	18	0.07	0.15	24	9	385	74	--	---	0.81	0.36	0.035	0.037	----	0.13	----
05/25/80	1	0.06	0.15	7	7	32	7	14	292	0.39	0.25	0.004	0.217	1.5	0.31	0.19
	3	0.15	0.17	24	8	265	70	--	633	0.81	0.39	0.018	0.135	32.3	0.73	0.46
	5	0.06	0.12	24	7	270	70	--	650	0.61	0.29	0.022	0.042	31.2	0.31	0.41
	8	0.03	0.13	24	7	270	69	8	---	0.50	0.29	0.020	0.027	33.9	0.35	0.38
	12	0.04	0.12	24	7	275	70	8	600	0.77	0.32	0.031	0.024	36.3	0.24	0.42
	16	0.04	0.18	30	7	284	72	--	---	1.04	0.38	0.056	0.067	39.0	0.23	0.36
06/08/80	1	0.06	0.59	6	3	34	8	26	267	0.73	0.14	0.009	0.113	2.4	0.58	0.13
	3	0.09	0.20	23	8	262	67	31	625	1.07	0.30	0.058	0.047	32.6	0.48	0.42
	5	0.07	0.14	23	7	270	69	16	583	0.81	0.30	0.064	0.036	32.9	0.55	0.39
	8	0.07	0.15	23	8	267	69	21	---	0.77	0.30	0.067	0.046	34.9	0.55	0.40
	12	0.07	0.12	25	8	272	69	18	600	1.77	0.32	0.069	0.046	31.2	0.48	0.42
	16	0.05	0.17	24	7	284	71	9	---	1.00	0.32	0.073	0.038	34.9	0.37	0.30
07/01/80	0	0.09	0.09	20	7	208	54	25	---	1.09	0.41	0.075	0.078	29.2	0.83	0.44
	1	0.08	----	19	6	208	54	36	633	1.11	0.45	0.126	0.080	23.9	0.83	0.42
	3	0.16	0.11	--	-	----	--	57	683	1.11	0.39	0.101	0.053	23.9	0.54	0.41
	5	0.18	0.20	20	7	208	54	49	717	1.36	0.39	0.127	0.042	24.2	1.28	0.42
	8	0.11	0.14	18	7	208	54	28	---	1.15	0.38	0.146	0.066	25.9	0.72	0.40
	12	0.10	----	18	7	206	54	20	550	1.16	0.39	0.135	0.095	25.9	0.65	0.46
	16	0.08	0.11	19	7	211	56	16	---	1.40	0.39	0.135	0.086	26.5	0.72	0.46
08/17/80	0	0.05	0.11	16	5	225	58	15	---	0.93	0.48	0.091	0.025	27.9	0.83	0.44
	1	0.08	0.11	17	6	223	58	21	783	0.95	0.48	0.089	0.015	24.9	0.73	0.43
	3	0.07	0.12	17	5	223	58	17	667	0.95	0.48	0.091	0.016	25.2	0.64	0.45
	5	0.08	0.10	17	6	225	58	17	583	0.95	0.52	0.091	0.013	23.9	0.61	0.34
	8	0.08	0.13	17	5	223	57	16	---	0.95	0.50	0.089	0.018	25.5	0.55	0.46
	12	0.05	0.12	--	-	----	--	13	708	0.97	0.52	0.093	0.018	25.9	0.66	0.44
	16	0.18	0.11	17	6	206	55	15	---	0.72	0.29	0.085	0.018	27.9	0.60	0.41
10/28/80	1	0.05	0.17	--	-	----	--	--	675	0.50	----	----	----	27.2	----	0.37
	3	0.05	0.16	--	-	----	--	--	---	0.52	----	----	----	22.8	----	0.29
	5	0.05	0.15	--	-	----	--	--	508	0.52	----	----	----	27.9	----	0.40
	8	0.07	----	--	-	----	--	--	---	0.59	----	----	----	27.6	----	0.36
	12	0.05	----	--	-	----	--	--	617	0.57	----	----	----	28.3	----	0.40
	16	0.05	0.19	--	-	----	--	--	---	0.54	----	----	----	24.2	----	0.25

## 1977 and 1978 stream chemistry.

Flow Rate																
Date	(m <sup>3</sup> d <sup>-1</sup> )	PP	DRP	TDP	PFe	DFe	PMn	ABS	Na	K	Ca	Mg	Date	PP	TDP	DRP
1978 Toolik Lake Main Inlet													1977 Toolik Main Inlet			
05/20	150337	0.18	0.03	0.23	1.24	1.81	0.10	0.83	38.7	22.0	397	84.3	05/20	0.37	0.24	0.11
05/23	50976	0.15	0.09	0.52	0.54	-	0.04	1.16	-	-	-	-	05/24	0.34	0.46	0.12
05/24	38016	0.12	-	0.28	0.38	2.35	0.03	1.01	55.2	30.9	255	58.0	05/27	0.31	0.33	0.05
05/26	13824	-	0.18	0.40	0.32	1.54	0.02	-	33.5	27.6	157	47.7	05/30	-	0.30	0.11
05/28	12960	0.08	-	0.36	0.25	1.50	0.01	1.12	52.6	24.8	147	45.2	05/31	0.98	0.51	0.13
05/30	171073	0.21	-	-	1.47	1.52	0.09	0.63	8.7	9.7	83	20.2	06/04	0.38	0.50	0.50
06/01	348194	0.21	-	0.27	1.43	3.42	0.18	0.83	12.2	13.6	110	33.7	06/08	0.26	0.25	0.09
06/03	241922	0.21	-	-	1.20	2.18	0.29	0.48	11.7	13.3	144	36.2	07/02	0.04	0.12	0.07
06/05	159841	0.15	0.09	-	0.79	2.42	0.12	0.60	16.5	10.7	140	34.1	07/16	0.04	-	-
06/07	184897	0.12	-	-	0.84	-	0.10	-	-	-	-	-	07/28	0.28	-	-
06/09	63072	0.09	-	0.16	0.57	0.93	0.05	0.48	4.3	2.3	34	8.2	08/22	0.05	0.13	-
06/12	99361	0.08	0.06	0.22	0.61	1.36	0.04	0.40	9.6	3.8	74	15.2	09/15	0.14	0.14	-
06/14	65664	0.05	0.05	0.18	0.48	1.06	0.03	0.41	5.2	3.8	56	13.2	1977 Toolik Inlet 2			
06/16	68256	0.08	0.06	0.18	0.63	-	0.05	0.40	-	-	-	-	05/10	1.26	1.20	0.58
06/19	69984	0.04	0.06	0.18	0.39	-	0.02	0.38	-	-	-	-	05/20	0.33	0.38	0.12
06/21	326594	0.08	0.07	0.20	0.29	1.41	0.06	0.65	26.1	5.6	127	34.1	05/27	0.35	0.48	0.08
06/25	-	0.05	0.08	0.16	0.41	-	0.03	0.64	16.5	5.1	132	34.1	06/08	0.26	0.25	0.09
06/27	-	0.04	0.02	0.16	0.36	-	-	-	-	-	-	-	07/02	0.02	0.11	0.05
06/28	61344	0.04	-	0.18	0.41	1.95	0.03	0.45	20.9	8.4	179	43.6	07/16	0.02	-	-
07/04	150337	0.05	0.07	0.17	0.61	1.07	0.06	-	13.9	3.3	96	25.5	08/22	0.18	0.11	-
07/06	82945	0.04	0.07	0.15	0.52	0.86	0.04	0.24	16.5	6.9	250	31.3	09/15	0.03	0.13	-
07/09	65664	-	-	0.16	-	0.82	-	0.38	28.7	4.3	110	31.7	1977 Toolik Outlet			
07/11	37152	0.05	-	-	0.30	1.50	0.03	0.48	32.6	4.1	137	25.1	05/10	0.14	0.27	-
07/13	50112	0.05	-	-	0.64	-	0.03	-	-	-	-	-	05/23	0.19	0.11	-
07/22	-	-	0.09	0.13	-	1.38	-	0.42	18.7	4.6	216	50.2	05/27	0.27	0.18	0.03
07/27	25920	0.04	0.06	0.11	0.82	1.25	0.03	0.38	28.3	4.6	218	52.7	06/08	0.33	0.31	0.08
07/31	-	-	0.03	0.13	-	0.88	-	0.28	27.4	5.9	225	55.5	07/02	0.13	0.07	0.10
08/01	14688	0.06	0.07	0.14	0.27	1.70	0.02	0.37	29.1	5.4	235	58.4	07/16	0.07	-	0.05
09/02	64800	0.05	0.04	0.12	0.39	-	0.07	22.2	5.1	248	63.8	-	07/28	0.07	-	-
1978 Toolik Lake Outlet													08/22	0.07	0.11	-
05/24	151201	-	-	-	-	-	-	-	-	-	-	-	09/15	0.08	0.13	-
05/26	77760	-	-	-	-	-	-	-	-	-	-	-				
05/28	37152	0.12	-	0.16	0.21	0.56	0.02	0.36	11.7	4.6	132	29.6				
05/30	104545	-	0.04	0.12	-	0.82	-	0.25	10.0	4.1	110	25.9				
06/01	443235	0.13	-	0.18	1.38	1.40	0.17	0.45	20.9	11.8	233	50.6				
06/03	-	0.10	0.07	0.25	0.70	-	0.11	0.56	-	-	-	-				
06/05	324002	0.13	-	0.23	0.86	1.40	0.16	0.57	17.8	13.8	189	51.4				
06/07	238466	0.14	-	0.14	0.77	-	0.20	-	-	-	-	-				
06/09	-	0.12	-	-	0.75	0.72	0.11	0.41	17.8	6.9	100	25.5				
06/12	146881	0.13	0.13	0.31	0.90	1.02	0.15	0.26	15.7	7.2	105	27.1				
06/14	112321	0.11	0.08	0.17	0.79	-	0.13	0.41	-	-	-	-				
06/16	87265	0.10	0.07	0.18	0.75	0.50	0.12	0.37	10.4	5.6	88	23.0				
06/19	-	0.10	-	-	0.84	0.86	0.11	0.37	25.2	8.7	167	42.4				
06/21	279938	0.10	-	-	0.91	0.84	0.09	0.35	20.4	8.4	174	45.2				
06/23	341282	-	-	-	-	-	-	-	-	-	-	-				
06/28	116641	0.09	-	-	0.59	0.86	0.08	-	27.0	29.7	382	54.3				
07/01	50976	0.11	0.06	0.15	0.57	0.54	0.09	0.37	17.4	5.1	110	28.4				
07/04	133921	0.09	0.06	0.10	0.61	2.04	0.07	0.28	15.2	4.9	86	19.7				
07/06	92449	0.09	0.08	0.14	0.63	1.65	0.07	0.35	-	-	115	28.8				
07/09	78625	-	0.07	0.13	-	0.63	-	0.39	25.2	6.1	127	32.9				
07/11	57024	0.07	0.07	-	0.86	0.59	0.08	-	26.5	8.4	172	44.4				
07/13	48384	0.14	0.14	-	0.52	-	0.08	-	-	-	-	-				
07/16	35424	0.05	0.05	-	0.56	-	0.06	-	-	-	-	-				
07/21	25920	0.06	0.10	0.13	0.61	0.70	0.12	-	14.8	6.6	167	40.7				
07/27	28512	0.05	-	0.20	0.27	0.56	0.08	0.34	19.1	7.4	179	44.8				
08/01	14688	0.08	0.06	0.15	0.34	2.26	0.18	0.38	11.7	2.8	56	14.4				
09/03	-	0.07	0.04	0.12	0.39	-	0.07	-	18.3	7.9	201	49.0				

## 1980 stream chemistry.

Date	Flow rate	PP	TDP	PFe	DFe	PMn	DMn	POC	DOC	WT	ABS	Si	Na	K	Ca	Mg
	(m <sup>3</sup> d <sup>-1</sup> )															
1980 Toolik Lake Main Inlet																
05/14	43200	0.50	1.08	2.31	0.73	0.05	0.67	83.3	1167	6.23	1.25	18.1	17.8	54.2	103	39.5
05/16	216001	0.41	0.69	1.50	1.79	0.17	1.97	108.3	942	4.24	1.12	20.8	18.3	30.2	172	50.2
05/18	256610	0.35	0.66	2.02	2.20	0.11	4.48	56.7	742	2.94	0.77	41.3	16.5	19.7	169	46.1
05/21	26784	0.14	0.53	0.79	1.67	0.07	0.33	79.2	650	1.55	0.66	24.9	17.4	15.3	162	41.1
05/25	55296	0.18	0.38	0.61	1.75	0.04	0.36	35.8	917	0.81	0.61	22.2	14.8	13.3	162	39.1
05/27	138241	0.15	0.41	0.95	1.25	0.08	0.27	34.2	550	1.22	0.56	20.8	13.9	13.0	152	38.7
05/30	63072	0.11	0.44	0.56	1.04	0.12	0.08	21.7	808	0.77	0.44	17.1	13.5	10.7	169	40.3
06/03	44928	0.06	0.28	0.86	1.13	0.02	0.05	17.5	533	0.50	0.42	15.5	14.8	7.9	152	37.0
06/08	217729	0.08	0.32	1.06	1.72	0.06	0.07	15.8	583	0.91	0.51	11.4	21.7	7.9	162	42.4
06/16	171937	0.03	0.21	0.79	0.98	0.04	0.13	43.3	583	1.00	0.69	25.2	20.0	5.6	145	37.4
06/23	152065	0.03	0.17	1.15	0.95	0.01	0.13	29.2	650	0.13	0.60	21.8	20.0	4.9	169	42.8
06/29	43200	0.04	0.11	0.82	1.04	0.02	0.19	36.7	558	0.48	0.50	16.1	19.1	5.4	199	47.7
07/05	386210	0.07	0.26	1.25	1.16	0.03	0.10	22.5	675	0.61	0.64	25.5	14.8	3.3	172	44.8
07/13	100225	0.04	0.10	0.47	1.49	0.04	0.12	-	533	0.57	0.54	31.2	23.5	3.3	213	52.7
07/20	50112	0.04	0.10	0.43	1.54	0.03	0.07	-	-	-	-	-	-	3.8	287	61.3
07/27	80353	0.04	0.15	0.48	1.56	0.03	0.12	30.0	625	0.52	0.48	29.9	23.9	3.6	267	66.6
08/03	114049	0.03	0.10	1.00	1.36	0.04	0.15	30.8	550	0.68	0.45	30.2	22.2	3.3	250	64.2
08/18	152929	0.02	0.11	0.75	1.13	0.03	0.13	9.2	533	0.58	0.51	34.9	17.4	4.6	279	63.8
08/23	56160	0.04	0.06	0.48	1.52	0.03	0.10	6.7	533	0.65	0.42	32.3	19.1	4.1	275	67.9
08/30	0	0.04	0.10	-	1.58	0.04	0.19	-	-	-	-	-	24.4	3.3	248	63.8
1980 Toolik Lake Inlet 2																
05/13	-	0.43	1.13	2.72	-	0.07	0.30	-	-	5.80	-	-	15.7	50.1	83	35.4
05/16	43200	-	0.79	2.31	1.36	0.15	0.58	100.0	1025	4.07	1.15	12.4	9.1	29.2	85	29.2
05/18	-	0.31	0.59	0.57	1.04	0.10	1.11	45.0	717	1.76	0.68	20.2	17.0	35.0	116	35.0
05/25	9504	-	0.41	0.75	1.20	0.05	0.10	25.0	475	1.16	0.52	12.1	13.9	30.0	104	30.0
05/27	18144	0.11	0.29	0.64	1.11	0.05	0.11	20.8	417	0.90	0.43	18.8	21.7	37.8	145	37.8
06/16	19872	0.02	0.10	1.22	-	-	0.11	38.3	508	0.40	0.58	33.9	22.2	46.9	167	46.9
06/23	18144	0.01	0.23	1.58	-	0.02	0.03	35.0	617	0.46	0.58	20.2	20.9	46.1	162	46.1
07/05	-	0.05	0.10	1.43	-	-	0.04	9.2	575	-	0.67	35.6	17.4	48.5	181	48.5
1980 Toolik Lake Outlet																
05/16	60480	0.08	0.17	0.23	0.79	0.03	0.24	23.3	700	0.47	0.44	35.3	27.4	9.0	336	82.7
05/18	-	0.07	0.30	0.82	0.84	0.05	0.82	28.3	558	1.29	0.54	26.5	20.9	13.8	245	63.8
05/21	64800	0.31	0.38	1.07	1.61	0.07	1.35	91.7	-	1.80	-	-	20.4	19.4	225	58.8
05/25	36288	0.27	0.48	1.06	1.22	0.12	0.70	50.0	725	1.61	0.67	49.4	21.3	17.4	221	59.2
05/27	126145	0.21	0.33	0.77	1.11	0.17	0.40	47.5	650	1.42	0.56	31.6	18.7	13.6	199	51.8
05/30	101089	0.17	0.39	1.09	1.02	0.13	0.15	50.0	475	1.36	0.37	13.1	25.2	10.5	171	39.1
06/03	59616	0.13	0.23	1.47	0.77	0.12	0.18	51.7	492	-	0.39	15.8	13.9	9.7	140	36.2
06/08	131329	0.13	0.25	0.75	0.75	0.09	0.07	51.7	550	1.20	0.36	17.8	19.1	8.7	157	40.3
06/16	298946	0.07	0.15	1.02	0.86	0.07	0.27	69.2	617	0.94	0.49	22.5	19.6	6.4	174	44.8
06/23	159841	0.08	0.10	0.79	0.57	0.08	0.16	48.3	517	0.98	0.41	25.5	20.9	6.4	206	52.7
06/29	126145	0.08	0.09	1.16	0.70	0.10	0.17	-	533	0.82	0.40	21.8	22.2	6.4	208	53.1
07/05	682564	0.10	0.19	0.73	0.43	0.09	0.03	26.7	583	-	0.41	18.5	16.5	6.1	206	52.7
07/13	190945	0.05	0.11	0.34	0.54	0.13	0.03	-	517	0.66	0.43	21.2	27.0	5.6	206	52.7
07/20	158113	0.21	0.11	0.38	0.47	0.08	0.04	-	517	-	-	-	22.6	5.1	206	53.1
07/27	131329	0.07	0.11	0.14	0.66	0.12	0.04	25.0	-	0.64	0.41	22.2	14.4	5.4	228	54.7
08/03	192673	0.05	0.09	-	0.88	0.10	0.03	-	525	-	0.39	21.2	22.6	5.9	230	55.5
08/18	188353	0.05	0.11	0.07	0.86	0.09	0.03	35.0	-	0.54	0.41	24.2	17.0	5.4	218	55.9
08/23	78625	0.07	0.13	0.20	0.84	0.10	0.06	-	-	0.62	0.38	23.5	17.4	5.4	225	57.6
08/30	-	0.06	0.09	0.54	0.59	0.04	0.11	24.2	-	0.88	-	-	25.2	4.3	225	56.8

## 1981 stream chemistry.

Flow rate		PP	TDP	PFe	DFe	PMn	DMn	WT	Na	K	Ca	Mg	
Date	(m <sup>3</sup> d <sup>-1</sup> )												
1981 Toolik Lake Main Inlet													
06/02	80353	0.08	0.15	0.75	1.99	0.06	0.05	0.53	17.8	6.1	130	30.9	
06/08	47520	0.05	0.14	0.54	1.38	0.02	0.02	0.38	13.9	5.9	150	32.9	
06/13	119233	0.05	0.18	0.98	1.90	0.07	0.05	0.66	17.4	5.9	130	30.9	
06/16	144233	0.06	0.17	0.63	1.18	0.04	0.08	0.71	14.4	5.1	127	28.8	
06/29	66528	0.05	0.09	0.39	1.00	0.03	0.05	0.70	62.6	4.6	240	45.7	
07/05	272162	0.09	0.10	1.27	1.07	0.24	0.10	1.50	38.7	4.1	167	41.5	
07/10	150337	0.03	0.15	-	0.86	0.04	0.04	0.48	23.5	2.6	162	40.7	
07/17	108865	0.03	0.08	0.43	0.73	0.04	0.07	0.53	15.2	2.6	179	44.8	
07/22	105409	0.06	0.23	-	0.95	0.02	0.08	0.57	18.3	2.3	191	49.0	
07/28	41472	0.08	0.11	0.66	1.00	0.02	0.09	0.53	16.5	3.3	225	52.7	
08/01	63936	0.04	0.06	0.61	1.29	0.05	0.15	0.59	24.4	2.6	235	57.6	
08/07	67392	0.03	0.06	0.38	1.09	0.02	0.11	0.57	24.8	3.6	272	59.6	
08/11	102817	0.05	0.11	0.66	1.25	0.03	0.11	0.85	21.3	2.8	228	54.3	
08/18	69984	0.03	0.05	0.47	1.20	0.02	0.08	0.51	30.9	4.9	284	65.8	
08/29	77760	-	-	0.73	1.07	-	0.07	-	23.9	2.6	252	62.1	
1981 Toolik Lake Inlet 2													
06/13	13824	0.05	0.21	0.75	0.73	0.05	0.03	0.78	22.6	29.4	172	43.2	
06/16	13824	0.05	0.15	0.47	0.81	0.04	0.04	0.62	22.6	2.8	152	40.3	
07/05	25920	0.06	0.10	1.47	0.91	0.08	0.01	1.18	20.9	2.0	147	40.3	
07/10	12960	0.03	0.08	0.18	0.95	0.04	0.03	0.68	23.9	2.0	176	46.9	
07/17	6048	0.03	0.12	0.72	0.68	0.04	-	3.29	17.0	2.0	201	51.8	
08/11	17280	0.05	0.11	0.95	1.09	0.07	-	1.10	23.5	2.3	194	54.3	
1981 Toolik Lake Outlet													
06/02	101089	0.12	0.20	0.90	1.20	0.25	0.23	1.11	20.0	9.2	145	35.8	
06/08	43200	0.17	0.25	0.84	1.06	0.21	0.08	1.25	14.8	9.0	145	35.8	
06/13	102817	0.12	0.15	0.63	0.68	0.14	0.10	0.81	14.4	6.4	152	36.6	
06/16	117505	0.12	0.18	0.75	0.64	0.10	0.19	0.85	16.5	5.6	169	40.7	
06/29	108001	0.09	0.08	0.50	0.54	0.19	0.13	0.69	22.2	6.9	270	53.5	
07/05	230689	0.09	0.50	0.70	0.47	0.13	0.11	0.77	20.9	5.4	211	52.2	
07/10	366338	0.10	0.09	0.50	0.45	0.12	0.05	0.94	22.2	5.1	206	51.4	
07/17	119233	0.06	0.10	0.41	0.38	0.09	0.04	0.69	14.8	4.9	208	50.2	
07/22	128737	0.09	0.06	0.38	0.32	0.09	0.03	0.77	17.4	4.1	208	51.4	
07/28	75168	0.15	0.08	1.50	0.50	0.29	0.11	2.42	17.4	4.9	213	51.4	
08/01	63936	0.07	0.10	0.36	0.32	0.13	0.03	0.71	20.9	4.3	213	51.4	
08/07	89857	0.06	0.08	0.27	0.34	0.05	0.03	0.53	23.9	4.1	218	52.7	
08/11	105409	0.06	0.11	0.16	0.32	0.04	0.03	0.45	21.3	2.8	228	54.3	
08/18	94177	0.06	0.14	0.21	0.32	0.06	0.05	0.47	28.3	4.1	223	55.1	
08/29	116641	-	-	0.30	0.29	-	0.02	-	22.6	4.1	221	54.7	

## APPENDIX B. SOLID PHASE CHEMISTRY

The data in this appendix are:

1. Surficial sediment chemistry (1977-1979).
2. 1978 and 1979 pH and Eh data.
3. Toolik Lake cores: vertical profiles from 1978 and 1979.

All concentrations are  $\text{mg g}^{-1}$  except as noted. "ORG" is the organic matter concentration (ashing at  $500^{\circ}\text{C}$ ), the prefix "TOT" signifies  $\text{LiBO}_2$  fusion data and the prefix "OX" signifies oxalate extraction.



## Surficial Sediment Chemistry (1977-1979)

All concentrations are mg g<sup>-1</sup>.

ID	Lake Depth (m)	Org	Tot-Al	Ox-Al	Tot-P	Ox-P	Tot-Fe	Ox-Fe	Tot-Mn	Ox-Mn
TL-001	4.0	210	48	-	1.89	-	84	-	3.2	-
TL-002	6.0	228	35	-	2.91	-	148	-	22.1	-
TL-003	4.0	238	52	3.3	1.78	0.56	36	37	0.4	0.3
TL-004	1.5	214	45	2.5	0.98	0.19	32	29	2.4	2.6
TL-005	1.5	75	44	1.2	0.86	0.10	18	8	0.5	0.5
TL-006	3.5	241	43	2.0	1.64	0.41	48	38	0.9	0.8
TL-007	7.0	192	36	2.0	4.09	1.63	130	142	32.6	-
TL-008	6.0	170	49	2.6	3.20	0.89	135	88	3.6	3.3
TL-009	4.0	225	50	2.4	2.20	0.46	34	22	0.4	0.4
TL-010	14.0	193	49	5.2	1.92	0.88	107	87	67	-
TL-011	14.0	158	68	7.6	1.97	0.99	86	90	44	-
TL-012	16.0	171	43	4.2	1.12	0.32	73	57	167	-
TL-013	4.5	287	43	-	1.20	-	17	-	0.6	-
TL-014	5.0	156	44	3.4	1.80	0.52	103	82	54	-
TL-015	7.0	185	40	2.8	2.28	0.89	134	125	51	-
TL-016	2.5	211	48	2.8	1.24	0.18	20	9	0.9	1.0
TL-017	5.0	203	50	3.0	1.24	0.19	21	6	0.2	0.3
M	18.0	177	48	4.4	1.76	0.57	87	57	66	62
CB1	5.5	241	43	4.5	1.97	0.48	74	53	0.8	1.2
TL-101	5.5	158	43	3.3	1.52	0.72	29	9	0.3	0.2
TL-102	5.5	148	40	2.9	0.95	0.38	32	9	0.3	0.1
TL-103	6.0	187	29	1.9	2.48	2.26	177	149	33	31
TL-104	10.0	139	56	3.8	1.70	0.89	40	12	0.4	0.4
TL-105	7.5	127	42	4.3	1.53	0.63	70	39	55	51
TL-106	7.0	139	40	3.7	1.62	0.71	140	97	37	35
TL-107	6.0	232	41	3.8	2.22	1.48	70	34	0.6	0.4
TL-108	3.0	149	45	4.2	1.75	0.80	45	18	0.8	0.6
TL-109	6.0	156	38	2.7	1.88	0.62	152	91	38	36
TL-110	9.0	149	54	5.7	2.03	0.84	94	59	62	60
TL-111	18.0	165	47	4.6	1.78	0.83	90	60	89	91
TL-112	12.0	177	42	2.2	2.19	2.06	174	139	12.0	11.5
TL-113	9.0	170	48	3.5	1.30	0.88	36	17	0.6	0.6
TL-114	6.0	228	38	3.7	2.55	0.97	90	78	1.3	1.4
TL-115	3.0	254	42	2.5	1.13	0.64	25	9	0.3	0.2

Org = organic content (ashing at 500 °C)

Tot = total analysis (lithium metaborate fusion)

Ox = oxalate extraction

1978 and 1979 pH and Eh(mv) data.

<u>depth</u>	<u>pH</u>	<u>Eh(mv)</u>	<u>depth</u>	<u>pH</u>	<u>Eh(mv)</u>	<u>depth</u>	<u>pH</u>	<u>Eh(mv)</u>
TL-010			TL-014			M		
0	6.90	475	0	6.12	286	0.5	6.18	413
1	6.90	485	1	6.05	316	1.5	6.02	473
3	6.60	255	3	6.78	141	2.5	6.32	473
5	6.90	60	5	7.09	64	3.5	6.61	463
7	7.10	65	7	7.11	36	4.2	6.83	223
10	7.00	75	10	7.00	47	5.0	7.09	133
15	7.00	95	15	6.90	71	6.0	7.19	53
			20	6.90	83	7.0	7.44	23
TL-011			TL-015			8.0	7.40	-7
0	6.25	357	0	6.05	403	9.0	7.45	-17
1	6.05	462	1	6.06	273	10.5	7.47	-17
3	6.50	232	3	7.02	43	11.5	7.45	-7
5	7.00	197	5	7.20	23	12.5	7.45	7
7	7.00	97	8	7.30	5	15.5	7.48	3
10	6.95	102	10	7.23	23	20.5	7.42	13
15	7.05	42	15	7.20	23	CB1		
20	6.85	62				0.5	6.4	106
TL-012			TL-016			1.5	6.7	203
0	-	170	0	6.90	243	2.5	7.3	-17
1	-	175	1	6.70	152	3.5	7.4	-42
3	-	205	3	6.20	155	4.5	7.4	-37
5	-	185	5	6.30	174	5.5	7.3	-67
7	-	70	7	-	182	6.5	7.1	-7
10	-	70	10	-	180	7.5	7.1	-7
15	-	70	20	-	183	8.5	7.0	3
20	-	55	25	-	185	9.5	6.9	33
TL-013			TL-017			10.5	6.9	33
0	6.00	149	0	5.83	324	11.5	6.9	33
1	6.00	201	1	6.40	211	12.5	6.9	43
3	6.30	179	3	6.50	175	13.5	6.8	43
5	6.40	172	5	6.45	174	14.5	6.8	43
7	6.40	168	7	6.48	184	15.5	6.7	53
10	6.40	173	10	6.45	175	16.5	6.7	63
15	6.40	184	15	6.50	184	17.5	6.7	63
20	6.20	182	20	6.52	164	18.5	6.6	43
						19.5	6.6	43
						20.5	6.7	43

# Toolik Lake cores: vertical profiles from 1978

Depth(cm) Org Tot-P Ox-P Tot-Fe Ox-Fe Tot-Mn Ox-Mn Tot-Al Ox-Al

## TL-010

00-01	193	1.92	0.88	107	87	67	-	49	5.2
01-03	181	1.58	0.55	109	78	79	87	52	4.6
03-05	168	1.76	0.78	138	163	81	101	49	4.2
05-07	140	4.54	3.12	150	158	63	80	56	3.9
07-10	100	3.10	2.32	76	67	23	33	75	6.8
10-15	117	3.14	2.34	84	81	23	31	71	7.4
15-20	127	3.16	-	74	-	19	-	71	-
20-25	147	3.16	2.22	63	60	16	24	72	7.9

## TL-011

00-01	158	1.97	0.99	86	90	44	37	68	7.6
01-03	134	1.43	0.47	173	113	37	-	112	4.3
03-05	130	1.94	0.46	249	129	6.6	3.8	76	3.6
05-07	101	3.22	1.45	147	61	2.5	2.3	112	5.5
07-10	87	2.34	1.21	94	50	0.7	0.8	130	6.8
10-15	92	2.74	1.63	101	69	0.7	0.9	124	7.9
15-20	57	2.49	1.90	112	65	0.6	-	125	6.4
20-25	36	1.14	0.89	52	25	0.3	-	137	5.2
25-30	36	-	0.65	-	10	-	0.3	-	4.4

## TL-012

00-01	171	1.12	0.32	73	57	167	-	43	4.2
01-03	184	1.22	-	76	-	149	-	-	-
03-05	169	1.14	-	90	-	146	-	-	-
05-07	158	2.56	-	155	-	24	-	-	-
07-10	138	3.78	-	122	-	13	-	-	-
10-15	109	2.64	-	100	-	6	-	-	-
15-20	114	2.39	-	104	-	6	-	-	-
20-25	134	2.58	-	108	-	6	-	-	-

## TL-013 (labelled T-4.5 in Chapter 3)

00-01	287	1.20	-	17	-	0.6	-	43	-
01-03	223	1.00	0.26	20	5	0.4	-	45	5.1
03-05	237	0.94	0.21	17	4	0.3	-	41	4.5
05-07	187	0.85	0.19	17	3	0.2	-	46	4.3
07-10	165	0.90	0.22	18	4	0.2	-	48	4.8
10-15	147	0.86	0.22	18	3	0.2	-	49	3.8
15-20	157	0.93	0.28	19	4	0.2	-	51	4.3
20-25	188	0.81	0.23	16	4	-	-	42	3.9

and 1979.

Depth(cm) Org Tot-P Ox-P Tot-Fe Ox-Fe Tot-Mn Ox-Mn Tot-Al Ox-Al

**TL-015 (labelled T-7 in Chapter 3)**

00-01	185	2.28	0.89	134	125	51	-	40	2.8
01-03	190	3.79	-	120	-	9	-	47	-
03-05	158	1.95	-	66	-	3	-	58	-
05-08	154	1.79	-	77	-	14	-	55	-
08-10	145	2.26	-	94	-	9	-	55	-
10-15	132	1.75	-	78	-	4	-	57	-
15-20	127	1.43	-	63	-	3	-	58	-

**CB1 (labelled T-5.5 in Chapter 3)**

00-01	241	1.97	0.48	74	53	0.76	1.2	43	4.5
01-02	249	2.61	1.04	133	106	1.64	2.0	34	3.4
02-03	250	2.99	1.61	122	89	1.04	1.2	36	3.3
03-04	244	2.94	1.10	102	66	0.81	0.8	43	3.9
04-05	248	2.97	1.66	101	73	0.78	1.0	43	3.9
05-06	239	2.14	0.33	70	40	0.49	0.6	47	4.5
06-09	235	1.51	0.34	48	25	0.32	0.3	52	5.2
09-12	209	1.24	0.23	39	17	0.23	0.3	58	4.9
12-15	181	1.05	0.27	26	14	0.20	0.2	57	4.4
15-18	176	0.97	0.19	24	11	0.19	0.2	55	4.0
18-21	175	0.90	0.17	23	11	0.18	0.2	54	4.0

**M (labelled T-18 in Chapter 3)**

00-01	177	1.76	0.57	87	57	66	62	48	4.4
01-02	131	1.41	0.38	81	48	131	60	42	3.8
02-03	149	1.25	0.28	81	47	121	56	45	4.2
03-04	129	1.15	0.22	89	54	138	66	43	3.6
04-4.5	148	1.16	0.40	257	206	32	26	30	2.1
4.5-5.5	133	2.63	1.38	123	71	13	12	65	4.3
5.5-6.5	121	3.52	2.41	128	80	6	9	68	5.6
6.5-7.5	123	4.49	2.57	158	103	8	12	60	5.6
7.5-8.5	111	2.75	1.98	96	74	4	7	72	7.3
8.5-10	102	2.11	1.30	79	51	3	5	77	7.0
10-11	91	2.83	2.17	114	87	4	7	69	5.8
11-12	86	2.70	2.09	112	83	4	7	75	5.6
12-13	100	2.51	1.76	94	67	4	6	73	6.6
15-16	100	1.99	1.22	84	55	3	4	77	6.4
20-21	112	2.58	1.80	115	82	4	6	72	7.8

## APPENDIX C. LEAD-210 DATA

The data in this appendix are:

1. Pb-210 data, cumulative mass data and cumulative Al data from 12 cores. Radium-226 data for one core are presented.
2. Porosity data: 1979 and 1980 cores.

The porosities were calculated assuming a solid sediment density of  $2.5 \text{ g cm}^{-3}$ . The standard deviation (counting statistics) are given for the Pb-210 concentrations. Analyses of major and minor elements for these cores are found in Appendix E.

Depth (cm)		Cumulative Mass	Cumulative Al	Pb-210 Activity	
Top	Bottom	(g cm <sup>-2</sup> )	(mg Al cm <sup>-2</sup> )	(dpm g <sup>-1</sup> )	(dpm (mg Al) <sup>-1</sup> )

#### T80-3.5C

0.00	1.08	0.053	2.60	10.88 ±0.34	0.222 ±0.010
1.08	2.00	0.166	8.64	3.36 ±0.11	0.059 ±0.003
2.00	3.21	0.325	17.48	2.06 ±0.06	0.037 ±0.002
3.21	4.20	0.539	28.45	1.37 ±0.04	0.029 ±0.001
4.20	5.51	0.793	41.18	1.61 ±0.08	0.031 ±0.002
5.51	6.30	1.012	52.88	1.90 ±0.10	0.034 ±0.002

#### T80-5.5C

0.00	0.90	0.048	1.43	14.22 ±0.53	0.474 ±0.023
0.90	1.84	0.144	4.75	13.97 ±0.62	0.358 ±0.019
1.84	2.70	0.236	8.90	9.93 ±0.25	0.195 ±0.008
2.70	3.77	0.342	14.65	3.78 ±0.13	0.066 ±0.003
3.77	4.66	0.457	21.24	2.95 ±0.10	0.051 ±0.002
4.66	5.65	0.573	28.10	2.38 ±0.12	0.040 ±0.002
5.65	6.69	0.701	35.80	2.44 ±0.09	0.041 ±0.002

#### T80-8.0C

0.00	1.06	0.048	2.15	20.23 ±0.46	0.450 ±0.017
1.06	1.81	0.137	6.10	11.08 ±0.36	0.252 ±0.011
1.81	3.02	0.245	10.74	5.85 ±0.25	0.139 ±0.007
3.02	4.43	0.394	17.09	2.69 ±0.12	0.062 ±0.003
4.43	5.25	0.520	22.70	2.48 ±0.14	0.052 ±0.003
5.25	6.16	0.619	27.37	2.17 ±0.10	0.047 ±0.003
6.16	7.12	0.744	33.66	2.16 ±0.10	0.040 ±0.002
7.12	8.49	0.910	42.53	2.09 ±0.10	0.039 ±0.002
8.49	9.43	1.073	51.85	2.03 ±0.09	0.032 ±0.002
9.43	10.43	1.203	60.28	2.10 ±0.09	0.031 ±0.002

#### T80-13.0C

0.00	1.08	0.055	3.16	25.08 ±0.75	0.432 ±0.018
1.08	2.06	0.164	9.24	10.82 ±0.50	0.204 ±0.011
2.06	3.13	0.302	15.63	3.67 ±0.14	0.087 ±0.004
3.13	4.59	0.482	24.65	3.25 ±0.18	0.057 ±0.004
4.59	5.59	0.643	33.98	3.04 ±0.16	0.052 ±0.003
5.59	6.75	0.793	42.57	3.17 ±0.13	0.057 ±0.003
6.75	7.74	0.949	52.40	2.50 ±0.15	0.035 ±0.002
7.74	9.19	1.139	66.46	2.29 ±0.09	0.031 ±0.002
9.19	10.06	1.332	80.59	1.92 ±0.10	0.027 ±0.002
10.06	11.18	1.496	92.17	1.97 ±0.10	0.028 ±0.002

Depth (cm)		Cumulative Mass	Cumulative Al	Pb-210 Activity	
Top	Bottom	(g cm <sup>-2</sup> )	(mg Al cm <sup>-2</sup> )	(dpm g <sup>-1</sup> )	(dpm (mg Al) <sup>-1</sup> )
T80-18.0D					
0.00	1.02	0.039	1.80	40.82 ±1.15	0.887 ±0.037
1.02	2.35	0.143	6.57	28.02 ±0.87	0.609 ±0.026
2.35	3.06	0.243	11.35	18.23 ±0.46	0.365 ±0.014
3.06	4.18	0.329	14.67	8.58 ±0.27	0.277 ±0.012
4.18	5.11	0.435	19.42	6.59 ±0.26	0.118 ±0.006
5.11	5.97	0.543	26.29	5.94 ±0.23	0.083 ±0.004
5.97	7.19	0.665	34.97	3.63 ±0.18	0.051 ±0.003
7.19	7.90	0.775	42.25	2.79 ±0.16	0.048 ±0.003
7.90	9.04	0.884	49.35	2.59 ±0.08	0.037 ±0.002
9.04	10.03	1.026	59.82	2.33 ±0.11	0.030 ±0.002
10.03	11.11	1.176	70.79	2.57 ±0.11	0.037 ±0.002

Depth (cm)		Ra-226 Activity	Ra-226 Activity
Top	Bottom	(dpm g <sup>-1</sup> )	(dpm (mg Al) <sup>-1</sup> )
T80-18.0D			
0.00	1.02	2.17 ±0.13	0.047
1.02	2.35	3.37 ±0.31	0.073
2.35	3.06	5.27 ±0.36	0.105
3.06	4.18	3.93 ±0.27	0.127
4.18	5.11	3.40 ±0.27	0.061
5.11	5.97	2.42 ±0.40	0.034
5.97	7.19	2.60 ±0.24	0.037

Depth (cm)		Cumulative Mass	Cumulative Al	Pb-210 Activity	
Top	Bottom	(g cm <sup>-2</sup> )	(mg Al cm <sup>-2</sup> )	(dpm g <sup>-1</sup> )	(dpm (mg Al) <sup>-1</sup> )

#### CB80-8.0C

0.00	1.05	0.048	2.95	20.94 ±0.78	0.343 ±0.016
1.05	2.10	0.147	9.14	12.93 ±0.47	0.202 ±0.009
2.10	3.09	0.257	16.31	7.89 ±0.30	0.118 ±0.006
3.09	4.25	0.392	25.56	5.21 ±0.20	0.076 ±0.004
4.25	5.05	0.531	35.24	2.83 ±0.09	0.040 ±0.002
5.05	5.88	0.658	44.23	2.96 ±0.12	0.042 ±0.002
5.88	6.95	0.808	54.64	2.03 ±0.08	0.030 ±0.001
6.95	7.77	0.959	64.93	2.24 ±0.08	0.033 ±0.002
7.77	8.63	1.096	74.48	2.18 ±0.10	0.031 ±0.002

#### T79A-5.5

0.00	1.17	0.051	2.40	13.78 ±0.36	0.293 ±0.012
1.17	2.56	0.186	8.76	9.65 ±0.22	0.205 ±0.008
2.56	3.96	0.375	17.86	4.73 ±0.14	0.097 ±0.004
3.96	5.33	0.590	28.70	2.49 ±0.09	0.048 ±0.002
5.33	6.57	0.798	39.79	1.74 ±0.12	0.032 ±0.003

#### T79C-6.0

0.00	0.89	0.046	1.48	12.09 ±0.45	0.378 ±0.018
0.89	2.12	0.170	5.90	10.77 ±0.43	0.283 ±0.014
2.12	3.25	0.338	13.36	9.63 ±0.35	0.193 ±0.009
3.25	4.52	0.539	25.74	7.24 ±0.30	0.102 ±0.005
4.52	5.63	0.759	40.06	3.77 ±0.18	0.064 ±0.003
5.63	6.71	0.973	52.87	2.96 ±0.14	0.049 ±0.002

#### T79D-10.0

0.00	1.05	0.056	3.40	24.20 ±0.89	0.397 ±0.019
1.05	2.25	0.198	12.45	13.90 ±0.53	0.214 ±0.010
2.25	3.42	0.380	24.45	4.67 ±0.15	0.070 ±0.003
3.42	4.43	0.575	37.59	1.53 ±0.05	0.022 ±0.001
4.43	5.60	0.803	52.73	--	--
5.60	6.75	1.068	70.53	1.26 ±0.08	0.018 ±0.002

#### T79E-7.5

0.00	1.12	0.044	2.31	19.94 ±0.68	0.383 ±0.017
1.12	2.15	0.150	7.93	15.78 ±0.61	0.292 ±0.014
2.15	3.20	0.285	15.42	6.38 ±0.24	0.112 ±0.005
3.20	4.61	0.476	25.87	2.56 ±0.10	0.048 ±0.002
4.61	6.01	0.736	38.24	--	--
6.01	6.94	0.968	48.09	2.81 ±0.13	0.041 ±0.003



Depth (cm)		Cumulative Mass	Cumulative Al	Pb-210 Activity	
Top	Bottom	(g cm <sup>-2</sup> )	(mg Al cm <sup>-2</sup> )	(dpm g <sup>-1</sup> )	(dpm (mg Al) <sup>-1</sup> )

# T79F-7.0

0.00	1.21	0.060	2.83	16.36 ±0.48	0.348 ±0.015
1.21	3.01	0.234	11.32	11.42 ±0.31	0.228 ±0.009
3.01	3.79	0.407	20.00	5.11 ±0.23	0.102 ±0.005
3.79	4.90	0.570	27.32	2.33 ±0.10	0.055 ±0.003
4.90	6.05	0.776	36.28	2.15 ±0.16	0.048 ±0.004

# T79G-6.0

0.00	1.10	0.048	2.66	16.17 ±0.50	0.294 ±0.013
1.10	2.47	0.166	9.20	11.55 ±0.41	0.206 ±0.010
2.47	3.51	0.293	16.64	7.34 ±0.27	0.118 ±0.006
3.51	4.92	0.442	25.91	3.76 ±0.17	0.061 ±0.003
4.92	5.86	0.602	35.89	--	--
5.86	6.86	0.744	43.28	0.78 ±0.04	0.012 ±0.001

Porosity data: 1979 and 1980 cores.

Depth	Porosity	Depth	Porosity	Depth	Porosity	Depth	Porosity	Depth	Porosity
T80-3.5C		T80-8.0C		T80-13.0C		CB80-8.0C		T79F-7.0	
0.5	0.961	0.5	0.964	0.5	0.960	0.5	0.963	0.6	0.960
1.5	0.948	1.4	0.956	1.6	0.955	1.6	0.961	2.1	0.950
2.6	0.935	2.4	0.956	2.6	0.938	2.6	0.952	3.4	0.938
3.7	0.906	3.7	0.954	3.9	0.947	3.7	0.947	4.3	0.926
4.8	0.916	4.8	0.958	5.1	0.947	4.6	0.939	5.5	0.928
5.9	0.918	5.7	0.951	6.2	0.942	5.5	0.937		
6.9	0.917	6.6	0.943	7.2	0.943	6.4	0.936		
7.9	0.913	7.8	0.943	8.5	0.934	7.4	0.935		
8.8	0.907	9.0	0.944	9.6	0.932	8.2	0.934		
9.6	0.905	11.2	0.941	10.6	0.935	9.2	0.927	T79G-6.0	
11.0	0.907	13.0	0.931			10.3	0.922	0.5	0.965
13.0	0.910	14.8	0.928	T80-18.0D		11.2	0.926	1.8	0.959
15.0	0.910	16.7	0.930			12.1	0.923	3.0	0.956
16.9	0.910	18.8	0.935	0.5	0.969	13.0	0.913	4.2	0.948
18.9	0.908	21.0	0.924	1.7	0.961	14.4	0.907	5.4	0.943
21.1	0.908	22.9	0.922	2.7	0.960	16.5	0.902	6.4	0.940
		24.9	0.920	3.6	0.965	18.5	0.855		
		27.0	0.902	4.6	0.950	20.5	0.788	T79D-10.0	
T80-5.5C		28.9	0.922	5.5	0.953	22.5	0.902	0.5	0.957
0.4	0.958	30.7	0.913	6.6	0.954	24.4	0.913	1.6	0.942
1.4	0.959	32.4	0.912	7.5	0.956	26.2	0.900	2.8	0.935
2.3	0.959	34.1	0.912	8.5	0.951	28.1	0.895	3.9	0.921
3.2	0.954			9.5	0.942			5.0	0.912
4.2	0.952	T80-11.0C		10.6	0.943	T79A-5.5		6.2	0.904
5.2	0.949	0.7	0.953	11.5	0.942	0.6	0.965		
6.2	0.950	1.8	0.953	12.3	0.933	1.9	0.952	T79E-7.5	
7.1	0.950	2.7	0.950	13.4	0.933	3.3	0.940	0.6	0.968
8.0	0.947	3.8	0.945	14.5	0.943	4.6	0.936	1.6	0.953
9.0	0.950	4.9	0.939	15.5	0.940	6.0	0.937	2.7	0.944
10.5	0.950	6.0	0.936	17.2	0.932			3.9	0.933
12.7	0.950	7.1	0.935	19.5	0.932	T79C-6.0		5.3	0.919
14.8	0.949	8.0	0.937	21.5	0.939	0.4	0.958	6.5	0.923
16.7	0.941	9.1	0.937	23.8	0.935	1.5	0.950		
18.6	0.942	10.3	0.937	26.1	0.935	2.7	0.936		
20.5	0.928	11.8	0.941	28.2	0.936	3.9	0.930		
22.4	0.907	13.7	0.941	30.4	0.937	5.1	0.921		
24.2	0.930			32.8	0.935	6.2	0.923		
26.1	0.935			35.7	0.910				
28.0	0.923								
29.9	0.907								
31.7	0.928								
33.7	0.918								

#### APPENDIX D. PORE WATER CHEMISTRY AND ASSOCIATED SOLID PHASE DATA

The data in this appendix are:

1. Pore water and solid phase analyses ( $\text{LiBO}_2$  fusion) for 8 cores.
2. 1980 and 1981 pore water DIC,  $\text{NH}_4^+$  and Si.
3. 1980 pH and Eh profiles.

All concentrations are  $\mu\text{M}$  unless otherwise noted. The P, Fe, Mn and major cation pore water data were obtained using squeezers loaded in  $\text{N}_2$  filled glove bags and the DIC,  $\text{NH}_4^+$  and Si data come from squeezers not loaded in a glove bag.

Core ID: CB80-8.0

Date of collection: 05/20/80

Overlying water depth (m): 8.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	4.1	150	44	20	83	430
01.0-02.0	7.8	132	31	65	104	1290
02.0-03.0	10.9	127	24	26	81	410
03.0-04.0	16.9	122	17	21	82	390
04.0-06.0	-	142	27	25	92	460
06.0-08.0	23.7	174	19	30	79	410
08.0-10.0	30.2	233	16	34	77	350
10.0-12.5	33.8	236	16	-	79	360
12.5-17.5	40.4	302	16	-	87	530
17.5-22.5	-	310	18	-	77	370

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg	Na
00.0-01.0	2.46	1.26	73	12.8	52	5.5	5.2	1.99
01.0-02.0	2.18	0.96	54	13.0	52	5.4	5.1	1.94
02.0-03.0	1.98	0.54	41	13.7	53	5.0	5.1	2.41
03.0-04.0	1.92	0.43	35	13.8	52	4.7	5.1	2.13
04.0-06.0	1.87	0.29	31	14.2	54	4.4	5.3	2.13
06.0-08.0	1.71	0.26	29	14.0	59	4.3	5.2	1.94
08.0-10.0	1.62	0.24	28	14.1	57	4.2	5.3	2.60
10.0-12.5	1.61	0.21	29	14.8	63	4.0	5.5	2.26
12.5-17.5	1.61	0.20	29	14.8	60	3.9	5.5	2.25
17.5-22.5	0.91	0.19	25	14.6	61	3.8	5.3	2.32
22.5-27.5	0.91	0.20	25	14.7	63	3.9	5.2	2.44

Core ID: T80-3.5A

Date of collection: 05/27/80

Overlying water depth (m): 3.5

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	1.5	19	9	18	53	254
01.0-02.0	2.9	26	14	18	59	282
02.0-03.0	5.2	53	22	23	67	644
03.0-04.0	4.9	58	26	19	57	304
04.0-06.0	6.5	40	23	-	-	-
10.0-12.5	-	36	24	-	-	-
12.5-17.5	-	52	19	-	58	237
17.5-22.5	4.0	56	26	19	51	269

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	1.57	1.20	47.6	11.0	43	4.3	4.5
01.0-02.0	1.28	0.58	34.7	11.9	45	3.3	4.7
02.0-03.0	0.96	0.39	25.4	10.6	37	2.2	4.2
03.0-04.0	0.71	0.30	16.8	9.4	32	1.8	3.8
04.0-06.0	0.78	0.36	17.1	11.1	39	2.4	4.7
06.0-08.0	0.78	0.41	18.8	12.7	47	2.8	5.3
08.0-10.0	0.81	0.45	20.1	14.2	55	2.9	5.8
10.0-12.5	0.76	0.41	20.0	15.2	60	3.0	6.0
12.5-17.5	0.72	0.34	18.7	14.6	55	2.8	5.8
17.5-22.5	0.72	0.32	18.7	13.9	55	3.2	5.8

Core ID: T80-5.5A

Date of collection: 05/28/80

Overlying water depth (m): 5.5

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	23.2	69	45	19	54	277
01.0-02.0	30.7	107	58	20	58	282
02.0-03.0	41.6	246	50	17	61	394
03.0-04.0	29.5	138	51	17	57	319
04.0-06.0	43.6	160	49	-	-	-
06.0-08.0	26.4	409	57	17	56	297
10.0-12.0	27.6	361	52	-	59	280
15.0-17.5	34.3	406	56	18	51	250
20.0-25.0	44.8	474	60	18	51	274
35.0-40.0	31.6	345	54	21	65	349

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	5.71	21.3	180	6.2	30	5.1	2.5
01.0-02.0	4.43	6.0	114	9.2	42	4.1	3.7
02.0-03.0	4.22	4.0	116	10.4	49	3.8	4.1
03.0-04.0	2.80	3.3	88	12.1	54	3.1	4.6
04.0-06.0	2.37	3.4	68	12.9	56	2.8	4.8
06.0-08.0	1.62	2.1	61	13.7	59	2.7	5.2
08.0-10.0	1.44	1.2	69	13.9	54	2.6	5.3
10.0-12.0	1.34	1.5	96	12.5	52	2.6	4.8
12.0-15.0	1.61	1.1	67	13.3	57	2.6	5.2
15.0-17.5	1.82	1.3	83	12.2	52	2.9	4.7
17.5-20.0	2.08	1.0	63	12.9	53	2.8	4.8
20.0-25.0	1.90	0.7	48	12.8	51	2.4	4.7
25.0-30.0	1.10	0.6	32	13.1	48	2.4	4.9
30.0-35.0	0.95	0.5	34	15.3	55	2.6	5.8
35.0-40.0	0.94	0.5	34	14.7	54	2.6	5.8

Core ID: T80-8.0A

Date of collection: 05/29/80

Overlying water depth (m): 8.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	0.8	5	1	16	64	277
01.0-02.0	0.7	5	29	20	60	250
02.0-03.0	1.6	5	99	26	66	299
03.0-04.0	1.2	5	188	25	69	432
04.0-06.0	3.1	5	284	19	63	274
06.0-08.0	14.7	19	339	19	60	277
10.0-12.0	28.2	150	360	19	61	457
15.0-17.5	11.2	163	339	19	52	262
20.0-25.0	19.3	232	343	19	54	277
35.0-40.0	19.4	165	283	20	59	334

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	1.71	39	67	9.9	46	5.2	4.1
01.0-02.0	1.40	113	60	8.7	41	4.0	3.4
02.0-03.0	1.44	105	65	9.0	41	3.4	3.4
03.0-04.0	1.21	135	59	8.4	40	3.1	3.1
04.0-06.0	1.55	89	71	9.8	45	3.1	3.6
06.0-08.0	5.00	27	133	9.6	45	3.2	3.6
08.0-10.0	5.94	14	105	11.8	60	2.5	4.3
10.0-12.0	3.64	7	80	15.3	71	1.9	5.4
12.0-15.0	3.02	8	94	14.9	70	1.8	5.2
15.0-17.5	2.88	8	111	14.1	68	1.8	4.9
17.5-20.0	4.10	10	124	12.9	68	2.0	4.6
20.0-25.0	2.90	7	102	14.6	73	1.8	5.1
25.0-30.0	1.78	4	68	17.2	77	1.9	5.9
30.0-35.0	2.78	7	111	13.4	67	1.8	4.6
35.0-40.0	1.70	5	88	15.8	72	2.1	5.7

Core ID: T80-11.0A  
 Date of collection: 05/30/80  
 Overlying water depth (m): 11.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	0.2	5	68	19	72	472
01.0-02.0	0.4	5	146	14	72	621
02.0-03.0	1.7	6	199	-	-	-
03.0-04.0	10.2	34	224	-	67	294
04.0-06.0	7.2	31	216	14	71	312
06.0-08.0	7.7	137	260	14	65	302
10.0-12.0	-	121	-	-	-	-
15.0-17.5	7.3	250	210	18	59	-
20.0-25.0	14.0	320	-	14	60	307
25.0-30.0	-	245	210	15	62	329
30.0-35.0	-	-	184	-	-	-

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	1.29	149	68	10.0	46	7.8	4.1
01.0-02.0	1.16	139	96	9.7	43	5.8	3.8
02.0-03.0	2.12	81	159	8.8	40	5.1	3.3
03.0-04.0	5.17	31	178	10.1	47	4.0	3.7
04.0-06.0	4.56	19	150	12.3	57	3.2	4.6
06.0-08.0	3.01	5	90	16.8	73	2.2	6.0
08.0-10.0	2.63	5	85	17.4	76	2.5	6.2
10.0-12.0	2.52	5	126	13.9	65	2.4	5.0
12.0-15.0	3.17	4	100	15.0	64	2.7	5.3
15.0-17.5	2.82	4	100	15.8	73	2.2	5.6
17.5-20.0	2.38	3	99	15.3	69	2.1	5.3
20.0-25.0	3.05	4	91	15.8	66	2.5	5.4
25.0-30.0	2.57	3	97	16.1	71	1.7	5.5
30.0-35.0	4.13	4	134	15.1	59	1.9	4.9



Core ID: T80-13.0A

Date of collection: 05/31/80

Overlying water depth (m): 13.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	0.4	5	0	16	70	269
01.0-02.0	0.4	5	3	13	67	254
02.0-03.0	0.6	5	17	19	59	230
03.0-04.0	0.8	5	33	14	55	210
04.0-06.0	0.7	5	74	15	62	267
06.0-08.0	6.2	25	240	19	62	272
08.0-10.0	4.6	23	223	14	57	252
10.0-12.5	2.3	27	243	14	59	264
12.5-17.5	6.5	89	259	13	56	264
22.5-27.5	12.5	115	268	13	57	274

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	2.27	21	96	13.3	60	5.8	5.3
01.0-02.0	1.21	104	119	9.6	47	4.1	3.8
02.0-03.0	1.33	169	77	11.1	49	3.8	3.8
03.0-04.0	1.37	143	76	11.2	53	3.5	4.1
04.0-06.0	1.43	103	86	12.8	60	3.2	4.5
06.0-08.0	1.59	40	162	11.9	64	3.0	4.2
08.0-10.0	2.85	17	134	15.0	63	2.3	5.2
10.0-12.5	3.54	7	115	16.8	72	1.9	5.8
12.5-17.5	3.02	6	102	16.9	83	1.8	5.9
17.5-22.5	3.46	7	121	17.5	72	1.8	5.2
22.5-27.5	3.38	6	112	15.5	73	1.9	5.3
27.5-32.5	2.85	5	115	15.2	78	1.9	5.2
32.5-37.5	2.59	4	89	17.9	88	1.8	6.1

Core ID: T80-18.0A  
 Date of collection: 05/22/80  
 Overlying water depth (m): 18.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	0.7	2	5	19	77	334
01.0-02.0	1.4	10	30	17	74	339
02.0-03.0	20.5	96	178	-	-	-
03.0-04.0	43.3	163	162	-	-	-
04.0-06.0	16.0	110	95	19	76	444
06.0-08.0	10.9	168	199	13	66	287
08.0-10.0	7.9	176	179	9	62	267
10.0-12.5	8.9	213	210	18	69	352
12.5-17.5	15.3	202	182	14	61	272
17.5-22.5	14.6	197	171	13	60	264

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
------------------------	---	----	----	---	----	----	----

Not analyzed

Core ID: T80-18.0B

Date of collection: 05/24/80

Overlying water depth (m): 18.0

Pore water chemistry (all concentrations are  $\mu\text{M}$ )

Depth interval (cm)	$\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
00.0-01.0	0.3	0	1	19	72	322
01.0-02.0	0.3	4	71	17	70	314
02.0-03.0	1.5	7	179	18	70	299
03.0-04.0	34.7	50	286	-	72	317
04.0-06.0	15.7	22	212	19	68	284
06.0-08.0	9.8	206	268	14	63	279
10.0-12.5	8.5	190	248	15	60	289
17.5-20.0	6.4	166	232	19	60	279
25.0-30.0	2.9	129	221	13	59	247
35.0-40.0	3.7	97	218	15	64	269

Solid phase chemistry (all concentrations  $\text{mg g}^{-1}$ )

Depth interval (cm)	P	Mn	Fe	K	Al	Ca	Mg
00.0-01.0	1.44	121	75	10.1	44	8.3	4.3
01.0-02.0	1.20	154	71	9.0	40	4.9	3.6
02.0-03.0	1.28	89	127	9.5	41	3.9	3.7
03.0-04.0	3.17	28	182	8.5	41	3.9	3.3
04.0-06.0	4.12	12	123	13.1	60	2.7	4.9
06.0-08.0	4.46	8	127	13.6	68	2.2	5.0
08.0-10.0	3.61	6	105	15.4	74	1.9	5.4
10.0-12.5	3.84	11	119	11.7	59	2.7	4.6
12.5-17.5	2.45	4	93	16.3	73	1.7	5.9
17.5-20.0	2.20	6	106	14.8	69	1.7	5.4
20.0-25.0	3.02	11	112	13.3	67	2.2	4.9
25.0-30.0	2.81	7	112	13.5	66	1.9	4.8
30.0-35.0	2.82	6	112	13.8	61	1.9	4.9
35.0-40.0	3.27	10	115	13.8	61	2.2	5.0

1980 and 1981 pore water DIC,  $\text{NH}_4^+$  and Si.

Depth	DIC	$\text{NH}_4^+$	Si	Depth	DIC	$\text{NH}_4^+$	Si	Depth	DIC	$\text{NH}_4^+$	Si
T80-18.0C				T80-5.5B				T81-3.0			
00.0-01.0	790	7.8	124	00.0-02.0	1740	8.3	178	00.0-01.0	1085	18.8	71
01.0-02.0	1060	7.7	143	04.0-06.0	1680	16.4	392	01.0-02.0	1166	20.7	101
02.0-04.0	1090	11.6	128	08.0-10.0	1880	34.8	388	02.0-03.0	1207	23.5	104
04.0-06.0	1440	18.3	120	12.5-17.5	2040	26.4	420	03.0-04.0	1200	32.6	101
06.0-08.0	1440	18.8	98	20.0-25.0	-	40.6	473	06.0-08.0	1352	43.8	146
08.0-10.0	1310	20.2	109	27.5-32.5	2190	48.2	416	10.0-12.0	-	43.8	225
10.0-12.5	1370	18.9	98	T80-8.0B				14.0-16.0	-	41.7	255
12.5-17.5	1310	24.1	90	00.0-02.0	1480	1.0	192	16.0-20.0	1713	45.4	188
22.5-27.5	1690	33.0	68	04.0-06.0	2270	4.9	321	T81-5.0			
32.5-37.5	1490	41.5	71	08.0-10.5	-	7.7	332	00.0-01.0	814	2.2	43
CB80-8.0B				15.0-20.0	2720	16.9	344	01.0-02.0	987	8.6	83
00.0-01.0	1410	16.3	109	25.0-30.0	-	14.8	247	02.0-03.0	1231	27.8	108
01.0-02.0	1600	17.1	117	T80-11.0B				03.0-04.0	1305	37.3	141
02.0-04.0	1430	25.1	117	00.0-02.0	1200	3.0	169	06.0-08.0	1511	82.7	214
04.0-06.0	1600	27.4	147	04.0-06.0	1620	7.7	147	10.0-12.0	-	111.1	225
06.0-08.0	1640	38.0	147	08.0-10.0	2400	13.1	139	14.0-16.0	1660	153.	267
08.0-10.0	1450	21.0	135	15.0-20.0	2870	30.7	143	18.0-20.0	-	157.	264
10.0-12.5	1640	33.1	165	25.0-30.0	2480	19.1	135	T81-7.0			
12.5-17.5	1390	28.7	184	37.5-42.5	3210	38.8	-	00.0-01.0	861	3.5	43
17.5-22.5	1310	34.6	244	T80-13.0B				01.0-02.0	1077	2.8	78
22.5-27.5	-	42.7	267	00.0-02.0	1485	3.0	83	02.0-03.0	1208	14.2	200
T80-3.5B				04.0-06.0	-	5.4	154	03.0-04.0	1108	19.8	196
00.0-02.0	1180	6.9	111	08.0-10.0	-	7.2	-	06.0-08.0	1236	30.6	189
04.0-06.0	-	16.1	255	15.0-20.0	2120	17.2	113	10.0-12.0	-	36.7	218
08.0-10.0	1990	21.4	284	25.0-30.0	-	19.6	109	14.0-16.0	-	49.7	270
12.5-17.5	1680	35.8	303	35.0-40.0	2240	32.3	113	18.0-20.0	-	66.7	282
20.0-25.0	1820	47.4	421	T81-18.0				00.0-01.0	669	4.2	120
								01.0-02.0	845	3.0	116
								02.0-03.0	1095	5.9	127
								06.0-08.0	1371	13.0	109
								12.0-14.0	1271	15.7	92
								18.0-20.0	1393	21.6	75
								26.0-28.0	1333	28.1	76
								03.0-04.0	-	-	135

## 1980 pH and Eh profiles.

depth	pH	Eh(mv)	depth	pH	Eh(mv)	depth	pH	Eh(mv)	depth	pH	Eh(mv)
T80-3.5A			T80-5.5B			T80-11.0B			T80-18.0B		
0.5	-	393	above 6.63	-		above 6.35	-		0.5	-	603
1.5	-	273	0.5	6.52	-	0.5	6.15	-	1.5	-	608
2.5	-	178	1.5	6.60	-	1.5	6.15	-	2.5	-	423
3.5	-	138	2.5	6.58	-	4.5	7.05	-	3.5	-	336
5.0	-	117	3.5	6.63	-	5.5	7.15	-	5.0	-	93
7.0	-	133	5.0	6.80	-	6.5	7.22	-	7.0	-	73
9.0	-	133	7.0	6.90	-	7.5	7.30	-	9.0	-	03
11.0	-	133	9.0	6.90	-	9.0	7.40	-	13.0	-	33
13.5	-	138	13.5	6.90	-	16.0	7.30	-	18.5	-	23
18.5	-	143	18.5	6.85	-	22.5	7.33	-	21.0	-	13
			22.5	6.90	-	27.5	7.35	-	26.0	-	03
									31.0	-	23
									36.0	-	13
T80-3.5B			T80-8.0A			T80-13.0A			CB80-8.0		
above 6.63	-		above 6.65	493		above 6.80	423				
0.5	6.52	-	0.5	6.60	563	0.5	6.60	433	0.5	7.02	253
1.5	6.60	-	1.5	6.60	553	1.5	6.50	418	1.5	7.00	123
2.5	6.58	-	2.5	6.60	553	2.5	6.50	563	2.5	6.98	93
3.5	6.63	-	3.5	6.80	528	3.5	6.65	553	3.5	6.98	83
5.0	6.80	-	5.0	6.90	528	5.0	6.65	543	5.0	6.92	93
7.0	6.90	-	7.0	7.02	293	7.0	7.10	343	7.0	6.88	103
9.0	6.90	-	9.0	7.30	113	9.0	7.50	123	9.0	6.82	118
13.5	6.90	-	11.0	7.72	28	11.0	7.65	63	13.0	6.83	118
18.5	6.85	-	13.0	7.80	23	13.5	7.75	23	18.5	-	103
22.5	6.90	-	16.0	7.80	18	18.5	7.73	3			
			18.5	7.70	23	23.5	7.75	3			
			31.0	7.60	33						
T80-5.5A			T80-11.0A			T80-18.0A					
0.5	-	218	0.5	-	443	0.5	6.40	580			
1.5	-	163	1.5	-	413	1.5	6.52	480			
2.5	-	53	2.5	-	313	2.5	7.00	200			
3.5	-	48	3.5	-	123	3.5	7.22	130			
5.0	-	53	5.0	-	33	5.0	7.60	90			
7.0	-	48	7.0	-	23	7.0	7.73	15			
9.0	-	48	9.0	-	23	9.0	7.75	10			
11.0	-	48	11.0	-	23	11.0	7.75	12			
13.0	-	53	13.0	-	23	13.5	7.75	10			
18.5	-	53	16.0	-	18	18.5	7.70	-5			
26.0	-	53	18.5	-	18	23.5	7.70	12			
36.0	-	53	26.0	-	23						

## APPENDIX E. TRACE ELEMENT DATA

The data in this appendix are:

1. Major and minor element concentrations: Toolik Lake surficial sediments.
2. Major and trace element concentrations: cores.

The cores used for analysis are the same ones used for Pb-210 analysis. Total ( $\text{LiBO}_2$ ) analyses include Al, Ca, Mg, K, Mn, Fe and P, and  $\text{HNO}_3$ -HCl digests were used for Ba, Zn, Ni, Co, Cu, Mo and Cr analyses.

Major and trace element concentrations: Toolik Lake surficial sediments.

Location	(mg g <sup>-1</sup> )								(ug g <sup>-1</sup> )							
	Al	Ca	Mg	K	Mn	Fe	P	org-C	CO3-C	N	Ba	Zn	Ni	Co	Cu	Cr
T80 - 3.5C	49	6.29	4.35	10.9	3.8	51	1.78	73.8	2.5	8.7	0.32	0.27	72	20	32	60
T80 - 5.5C	30	5.21	2.72	6.8	11.5	183	6.00	62.5	3.5	6.9	0.85	0.16	61	26	27	40
T80 - 8.0C	45	4.44	3.93	9.8	48	69	1.79	49.0	4.1	6.2	0.68	0.23	82	26	35	42
T80 -13.0C	58	5.90	4.99	12.6	23	97	2.34	58.7	4.0	6.8	0.44	0.29	112	36	50	54
T80 -18.0C	46	7.04	4.18	9.8	129	79	1.72	55.0	5.6	6.5	2.60	0.30	126	29	49	56
CB80- 8.0C	61	5.64	4.91	12.8	1.5	67	2.63	90.6	2.7	7.2	0.24	0.19	48	20	42	71
T79A- 5.5	47	4.96	4.20	11.0	0.5	24	1.89	85.9	1.7	10.4	0.18	0.13	42	7	27	50
T79C- 6.0	32	5.91	2.95	7.4	38	142	2.26	72.2	5.1	7.5	1.33	0.16	64	52	23	50
T79D-10.0	61	3.74	5.15	13.4	0.5	48	2.24	63.9	1.7	7.1	0.22	0.19	45	12	40	48
T79E- 7.5	52	5.16	4.37	11.1	13.8	67	1.90	62.0	3.2	7.8	0.45	0.24	92	24	40	42
T79F- 7.0	47	4.88	4.08	10.7	27	95	1.88	55.1	3.8	6.5	0.72	0.28	116	40	41	48
T79G- 6.0	55	4.82	4.41	11.6	1.3	76	2.59	89.9	2.6	9.8	0.22	0.25	55	18	42	26
Mean	49	5.3	4.2	10.7	25	83	2.4	68	3.4	7.6	0.7	0.22	76	26	37	51
SD	10	0.9	0.7	2.0	36	43	1.2	14	1.2	1.3	0.7	0.06	29	12	9	9

## Major and trace element concentrations: cores.

Core	Depth (cm)	(mg g <sup>-1</sup> )								(ug g <sup>-1</sup> )							
		Al	Ca	Mg	K	Mn	Fe	P	org-C	CO3-C	N	Ba	Zn	Ni	Co	Cu	Mo
T80 - 8.0C	0.53	45	4.44	3.93	9.8	48	69	1.79	49.0	4.1	6.2	0.68	0.23	82	26	35	2.5
	1.43	44	4.49	3.66	9.7	75	67	1.63	44.3	4.5	5.0	1.03	0.20	69	26	38	2.9
	2.41	42	4.12	3.29	9.3	124	63	1.37	32.2	4.7	4.0	2.91	0.20	62	22	35	5.5
	3.73	43	3.35	3.29	9.4	142	58	1.16	30.1	5.0	3.9	5.34	0.20	61	22	30	5.3
	4.84	48	3.48	3.61	10.3	99	66	1.25	34.9	4.6	3.9	4.02	0.19	68	40	28	4.2
	5.71	46	3.57	3.45	9.8	46	115	1.96	42.8	3.4	4.4	2.49	0.20	63	44	46	2.7
	6.64	54	2.85	3.89	11.1	14	122	3.92	37.8	1.6	3.9	1.30	0.22	69	26	35	2.7
	7.81	53	3.04	4.01	11.4	15	131	5.84	35.8	1.6	3.5	1.76	0.24	67	23	40	2.9
	8.96	63	2.67	4.89	14.1	10	93	4.09	--	--	--	1.24	0.22	70	24	44	2.7
	9.89	67	2.34	5.14	14.8	9	93	4.14	32.9	0.9	3.8	1.04	0.25	75	26	43	2.4
	16.69	63	2.27	4.64	13.6	10	117	3.51	31.7	1.2	3.5	0.89	0.31	80	27	53	2.6
	24.93	71	2.39	5.12	15.7	5	77	2.54	--	--	--	0.84	0.42	102	25	62	1.7
	34.10	75	2.59	5.94	16.6	4	71	1.80	--	--	--	0.64	0.25	86	25	52	2.4
T80 - 5.5C	0.45	30	5.21	2.72	6.8	11.5	183	6.00	62.5	3.3	6.9	0.85	0.16	61	26	27	-
	1.37	39	4.56	3.63	9.0	8.3	134	5.28	63.2	3.1	7.0	0.66	0.20	72	22	38	-
	2.27	51	3.71	3.98	11.3	3.7	82	3.28	59.8	1.7	7.2	0.44	0.28	79	21	48	-
	3.23	57	3.34	4.59	12.2	3.1	64	2.33	59.0	1.2	7.1	0.49	0.32	78	18	52	-
	4.22	58	3.15	4.52	12.6	2.2	61	2.23	55.0	1.1	6.2	0.44	0.43	75	15	52	-
	5.16	60	3.04	4.79	13.0	2.0	51	1.68	50.8	0.9	6.2	0.39	0.35	76	16	52	-
	6.17	60	3.02	4.81	13.1	1.9	53	1.52	--	--	--	0.42	0.39	81	18	52	-
T79C-6.0	0.45	32	5.91	2.95	7.4	37.6	142	2.26	72.2	5.1	7.5	1.33	0.16	64	52	23	2.8
	1.51	38	4.79	3.27	8.3	8.9	167	4.85	--	--	--	0.74	0.16	42	30	24	1.8
	2.69	50	3.57	4.08	10.6	2.7	80	2.89	--	--	--	0.42	0.23	51	22	36	1.7
	3.89	71	3.12	4.61	12.1	1.4	61	2.21	--	--	--	0.33	0.25	71	25	40	2.0
	5.08	59	2.98	4.70	12.4	1.4	51	2.00	--	--	--	0.35	0.26	60	17	40	0.9
	6.17	61	2.93	4.84	12.6	1.1	48	1.77	--	--	--	0.35	0.29	65	19	42	1.5

Core	Depth (cm)	(mg g <sup>-1</sup> )								(ug g <sup>-1</sup> )							
		Al	Ca	Mg	K	Mn	Fe	P	org-C	CO3-C	N	Ba	Zn	Ni	Co	Cu	Cr
T80-18.0D	0.5	46	7.04	4.18	9.8	129	79	1.72	55.0	5.6	6.5	2.60	0.30	126	29	49	56
	1.7	46	4.48	3.68	9.4	155	75	1.44	47.7	5.6	5.5	6.00	0.20	64	25	41	39
	2.7	50	3.90	4.06	10.4	91	111	1.40	47.2	5.0	6.0	5.04	0.18	63	88	40	44
	3.6	31	4.23	2.47	6.3	23	229	1.93	54.4	4.2	4.4	2.81	0.16	44	32	30	36
	4.6	56	3.05	4.45	11.5	13	153	3.53	47.8	2.0	5.7	1.34	0.26	59	27	51	49
	5.5	72	2.50	5.43	15.2	8	93	3.08	61.3	1.7	6.2	0.75	0.32	71	31	61	51
	6.6	71	2.28	5.15	14.4	10	132	4.01	50.2	1.9	4.9	0.78	0.30	75	38	57	46
	7.5	58	2.45	4.19	11.6	13	185	5.79	51.2	2.2	4.4	1.09	0.32	72	46	50	52
	8.5	69	2.14	4.94	14.0	9	131	4.23	--	--	--	0.71	0.30	77	38	53	56
	9.5	78	1.85	5.77	16.8	5	87	2.86	49.6	2.2	5.1	0.59	0.33	82	32	62	56
	10.6	69	--	--	15.7	6	108	3.31	--	--	--	--	--	--	--	--	--
	11.5	68	2.01	5.21	14.8	8	130	3.78	--	--	--	0.69	0.30	75	36	57	55
	12.3	75	--	--	17.7	5	91	2.43	--	--	--	--	--	--	--	--	--
	13.4	81	1.67	6.14	18.2	4	90	2.38	42.5	2.0	4.4	0.52	0.26	85	34	57	63
	14.5	61	--	--	15.6	5	103	2.68	--	--	--	--	--	--	--	--	--
	15.5	52	1.83	4.89	14.2	7	136	3.18	--	2.1	--	0.56	0.28	80	40	52	51
	17.2	67	--	--	17.1	5	97	2.38	42.8	--	4.4	--	--	--	--	--	--
	23.8	58	2.01	4.84	14.3	6	119	2.93	52.0	2.6	5.3	0.56	0.43	94	38	65	53
	28.2	56	2.06	4.84	14.5	6	122	3.09	46.2	2.7	--	--	--	--	--	--	--
	30.4	--	--	--	--	--	--	--	--	--	--	0.55	0.42	100	33	66	56
	35.6	77	1.91	6.40	19.9	3	86	2.38	33.5	1.6	3.6	0.46	0.26	75	27	56	52



## Major element concentrations: cores.

All concentrations are mg g<sup>-1</sup>

Core	(cm)	Al	K	Mn	Fe	P	Core	(cm)	Al	K	Mn	Fe	P
T80 - 3.5C	0.5	49	10.9	3.8	51.4	1.78	T79C- 6.0	0.4	32	7.4	37.6	142	2.26
	1.5	57	12.8	0.7	31.1	1.52		1.5	38	8.3	8.9	167	4.85
	2.6	55	12.8	0.6	27.9	1.39		2.7	50	10.6	2.7	80	2.89
	3.7	48	11.5	0.4	21.3	1.09		3.9	71	12.1	1.4	61	2.21
	4.8	52	12.5	0.4	20.9	1.05		5.1	59	12.4	1.4	51	2.00
	5.9	56	13.9	0.6	22.4	1.03		6.2	61	12.6	1.1	48	1.77
	8.8	62	14.1	0.4	21.4	1.02	T79D-10.0	0.5	61	13.4	0.52	48	2.24
	15.0	61	13.7	0.4	22.9	0.83		1.6	65	14.4	0.34	35	1.95
	21.1	62	14.0	0.4	23.1	0.81		2.8	67	14.9	0.32	30	1.83
T80 -13.0C	0.5	58	12.6	23	97	2.34		3.9	68	15.2	0.28	27	1.71
	1.6	53	11.5	84	89	1.97		5.0	65	15.6	0.25	30	1.61
	2.6	42	9.5	216	65	1.22		6.2	69	15.6	0.25	26	1.56
	3.9	57	12.4	97	87	1.54	T79E- 7.5	0.6	52	11.1	13.8	67	1.90
	5.1	59	12.6	97	88	1.43		1.6	54	11.8	16.7	68	1.84
	6.2	56	11.2	27	189	1.68		2.7	57	12.3	30.4	68	1.75
	7.2	72	15.0	11	126	2.78		3.9	53	11.6	66.1	87	1.50
	8.5	75	16.3	9	117	3.28		5.3	43	9.5	12.8	223	2.72
	9.6	70	15.5	9	135	3.82		6.5	42	9.6	16.6	217	3.28
	10.6	71	14.9	9	125	3.79	T79F- 7.0	0.6	47	10.7	27	95	1.88
T79A- 5.5	0.6	47	11.0	0.45	24.0	1.89		2.1	50	10.7	39	89	1.76
	1.9	47	11.1	0.19	17.9	1.45		3.4	50	10.2	57	127	1.50
	3.3	49	11.2	0.16	16.5	1.13		4.3	42	8.3	14	210	2.68
	4.6	52	12.0	0.13	16.9	1.07		5.5	45	9.2	11	214	3.85
	6.0	55	12.0	0.14	17.4	1.11							

Core	(cm)	Al	K	Mn	Fe	P
T79G-6.0	0.6	55	11.6	1.29	76	2.59
	1.8	56	12.5	0.72	60	2.45
	3.0	62	13.2	0.54	52	2.39
	4.2	62	13.5	0.51	45	2.13
	5.4	63	14.0	0.47	42	2.08
	6.4	63	13.9	0.50	42	2.05
CB80-8.0C	0.5	61	12.8	1.51	67	2.63
	1.6	64	13.4	1.04	46	2.38
	2.6	67	13.4	0.58	39	2.31
	3.7	69	14.1	0.59	38	2.33
	4.6	71	14.3	0.48	32	2.23
	5.5	71	14.3	0.49	32	2.06
	6.4	68	14.1	0.51	30	1.88
	7.4	68	13.7	0.43	28	1.81
	8.2	71	14.5	0.33	29	1.94